

Chapter 4

The Methodology of Statistical Mechanics

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We develop the basic methodology of statistical mechanics and provide a microscopic foundation for the concepts of temperature and entropy.

4.1 Introduction

We now will apply the tools and concepts of thermodynamics and probability which we introduced in Chapters 2 and 3 to relate the microscopic and macroscopic descriptions of thermal systems. In so doing we will develop the formalism of *statistical mechanics*. To make explicit the probabilistic assumptions and the type of calculations that are done in statistical mechanics we first discuss an isolated system of non-interacting spins. The main ideas that we will need from Chapter 3 are the rules of probability, the calculation of averages, and the principle of least bias or maximum uncertainty.

Consider an isolated system of $N = 5$ noninteracting spins or magnetic dipoles with magnetic moment μ and spin $1/2$ in a magnetic field B . Each spin can be parallel or antiparallel to the magnetic field. The energy of a spin parallel to the magnetic field is $\epsilon = -\mu B$, and the energy of a spin aligned opposite to the field is $\epsilon = +\mu B$. We will consider a specific case for which the total energy of the system is $E = -\mu B$. What is the mean magnetic moment of a given spin in this system? The essential steps needed to answer this question can be summarized as follows.

1. *Specify the macrostate and accessible microstates of the system.* The macroscopic state or *macrostate* of the system corresponds to the information that we know. In this example we know the total energy E and the number of spins N .

The most complete specification of the system corresponds to the enumeration of the *microstates* or *configurations* of the system. For $N = 5$ there are $2^5 = 32$ microstates specified by the

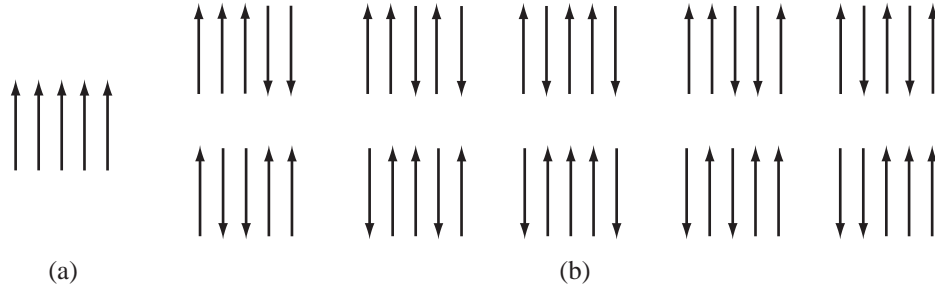


Figure 4.1: (a) Example of an inaccessible microstate corresponding to the macrostate specified by $E = -\mu B$ and $N = 5$. (b) The ten accessible microstates. Spin #1 is the left most spin.

orientation of each of the N spins. Not all of the 32 microstates are consistent with the information that $E = -\mu B$. For example, the microstate shown in Figure 4.1(a) is not allowed, that is, such a microstate is inaccessible, because its energy is $E = -5\mu B$. The *accessible* microstates of the system are those that are compatible with the macroscopic conditions. In this example ten of the thirty-two total microstates are accessible (see Figure 4.1(b)).

2. *Choose the ensemble.* We calculate averages by preparing a collection of identical systems all of which satisfy the macroscopic conditions $E = -\mu B$ and $N = 5$. In this example the ensemble consists of ten systems each of which is in one of the ten accessible microstates.

What can we say about the relative probability of finding the system in one of the ten accessible microstates? Because the system is isolated and each microstate is consistent with the specified macroscopic information, we assume that each microstate in the ensemble is equally likely. This assumption of *equal a priori probabilities* implies that the probability P_s that the system is in microstate s is given by

$$P_s = \frac{1}{\Omega}, \quad (4.1)$$

where Ω represents the number of microstates of energy E . This assumption is equivalent to the principle of least bias or maximum uncertainty that we discussed in Section 3.4.1. For our example we have $\Omega = 10$, and the probability that the system is in any one of its accessible microstates is $1/10$. The macroscopic constraints, the microstates consistent with these constraints, and the relative probabilities of the microstates specify the ensemble. Here the constraints are the values of E and N and the ten accessible microstates are given in Figure 4.1(b) with the probabilities in (4.1).

3. *Calculate the mean values and other statistical properties.* In this simple example we will calculate the mean value of the orientation of spin #1 (see Figure 4.1(b)). Because s_1 assumes the value ± 1 , we have

$$\bar{s}_1 = \sum_{i=1}^{10} P_i s_{1,i} \quad (4.2a)$$

$$= \frac{1}{10} [6(+1) + 4(-1)] = \frac{2}{10} = \frac{1}{5}. \quad (4.2b)$$

The sum is over all the accessible microstates and $s_{1,i}$ is the value of spin #1 in the i th member of the ensemble. We see from (4.2b) that the mean value of s_1 is $\bar{s}_1 = 1/5$. The corresponding mean magnetic moment of spin #1 is $\mu\bar{s}_1 = \mu/5$.

Problem 4.1. Simple example

- (a) What is the mean value of spin #2 in the above example? Why is its mean value not zero?
- (b) What is the probability p that a given spin points up?
- (c) What is the probability that if spin #1 is up, then spin #2 also is up? □

There is a more direct way of calculating \bar{s}_1 in this case. Because the magnetization of the system is $M = \mu$, three out of the five spins are up. The equivalency of the spins implies that the probability of a spin being up is $3/5$. Hence, $\bar{s} = (1)(3/5) + (-1)(2/5) = 1/5$. What is the implicit assumption that we made in the more direct method?

Problem 4.2. Counting microstates

- (a) Consider $N = 4$ noninteracting spins with magnetic moment μ that can point either parallel or antiparallel to the magnetic field B . If the total energy $E = -2\mu B$, what are the accessible microstates and the probability that a particular spin is up or down?
- (b) Consider $N = 9$ noninteracting spins with total energy $E = -\mu B$. What is the number of up spins, the number of accessible microstates, and the probability that a particular spin is up or down? □

Problem 4.3. Probability of particles moving in same direction

Consider a one-dimensional ideal gas consisting of $N = 5$ particles each of which has the same speed v , but can move in one of two directions with equal probability. The velocity of each particle is independent. What is the probability that all the particles are moving in the same direction? □

The example that we have just considered is an example of an *isolated system*. In this case the system of spins has fixed values of E , B , and N . An isolated system cannot exchange energy or matter with its surroundings nor do work on another system. The macrostate of an isolated system of particles is specified by E , V , and N (B instead of V for a magnetic system). Isolated systems are conceptually simple because all the accessible microstates have the same probability. We will learn that isolated systems are described by the *microcanonical ensemble*. (see Section 4.5).

4.2 A Simple Example of a Thermal Interaction

Now that we have an idea of how we can do probability calculations for an isolated system, we next consider some simple systems that can exchange energy with another system. We will see that for nonisolated systems, the probability of each microstate is not the same.

We know what happens when we place two bodies at different temperatures into thermal contact with one another – energy is transferred from the hotter to the colder body until thermal

microstate	red	white	blue
1	1	1	1
2	2	0	1
3	2	1	0
4	1	0	2
5	1	2	0
6	0	1	2
7	0	2	1
8	3	0	0
9	0	3	0
10	0	0	3

Table 4.1: The ten accessible microstates of a system of $N = 3$ distinguishable particles with total energy $E = 3$. Each particle may have energy 0, 1, 2, ...

equilibrium is reached and the two bodies have the same temperature. We now consider a simple model that illustrates how statistical concepts can help us understand the transfer of energy and the microscopic nature of thermal equilibrium.

Consider a system of N noninteracting distinguishable particles such that the energy of each particle is restricted to integer values, that is, $\epsilon_n = 0, 1, 2, 3, \dots$. We can distinguish the particles by their colors, or we can assume that the particles have the same color, but are fixed on lattice sites. For reasons that we will discuss in Section 6.9, we will refer to this model system as an Einstein solid.¹

Consider an Einstein solid with $N = 3$ particles (with colors red, white, and blue) in an isolated box and total energy $E = 3$. For these small values of N and E , we can enumerate the accessible microstates by hand. The ten accessible microstates of this system are shown in Table 4.1. Because the energy is specified, the ten accessible microstates are equally probable.

Problem 4.4. Simple Einstein solid

Consider an Einstein solid composed of N particles with total energy E . The general expression for the number of microstates of this system is

$$\Omega = \frac{(E + N - 1)!}{E!(N - 1)!}. \quad (4.3)$$

- Verify that (4.3) yields the correct answers for $N = 3$ and $E = 3$.
- What is the number of microstates for an Einstein solid with $N = 4$ and $E = 6$?
- Suppose that $N = 3$ and $E = 3$ and the particles are labeled red, white, and blue. What is the probability that the red particle has energy equal to one?
- Given that the red particle has energy 1, what is the probability that the blue particle has energy 2? \square

¹These particles are equivalent to the quanta of the harmonic oscillator, which have energy $E_n = (n + \frac{1}{2})\hbar\omega$, where $\hbar = h/2\pi$, and h is Planck's constant. If we measure the energies from the lowest energy state, $\frac{1}{2}\hbar\omega$, and choose units such that $\hbar\omega = 1$, we have $\epsilon_n = n$.

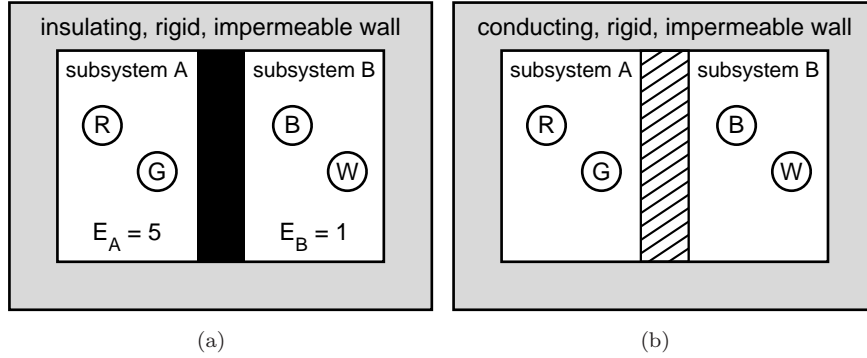


Figure 4.2: An isolated composite system consisting of two subsystems, each with two distinguishable particles. In (a) the wall between the two subsystems is insulating, rigid, and impermeable. In (b) the wall is conducting, rigid, and impermeable. The total energy of the composite system is six.

Now that we know how to enumerate the number of microstates of an Einstein solid, consider an isolated system of $N = 4$ particles that is divided into two *subsystems*. A system consisting of two or more subsystems is called a *composite system*. In this case the latter is surrounded by insulating, rigid, impermeable outer walls so that its energy, volume, and number of particles is fixed. It also is initially separated by a similar partition (see Figure 4.2) so that there can be no change in the energy, number of particles, and the volume of each subsystem. Subsystem A consists of two particles, R (red) and G (green), with $E_A = 5$; subsystem B consists of two particles, B (black) and W (white), with energy $E_B = 1$. The total energy E_{tot} of the isolated composite system consisting of subsystem A plus subsystem B is

$$E_{\text{tot}} = E_A + E_B = 5 + 1 = 6. \quad (4.4)$$

The accessible microstates for the isolated composite system are shown in Table 4.2. We see that subsystem A has $\Omega_A = 6$ accessible microstates and subsystem B has $\Omega_B = 2$ accessible microstates. The total number of microstates Ω_{tot} accessible to the composite system is

$$\Omega_{\text{tot}} = \Omega_A \times \Omega_B = 6 \times 2 = 12. \quad (4.5)$$

The partition is an internal constraint that prevents the transfer of energy from one subsystem to another and in this case keeps $E_A = 5$ and $E_B = 1$. (The internal constraint also keeps the volume and number of particles in each subsystem fixed.)

We now consider a simple example of a thermal interaction. Suppose that the insulating, rigid, impermeable partition separating subsystems A and B is changed to a conducting, rigid, impermeable partition (see Figure 4.2). The rigid partition maintains the volumes V_A and V_B , and hence the single particle energies are not changed. Because the partition is impermeable, the particles cannot penetrate the partition and go from one subsystem to the other. However, energy can be transferred from one subsystem to the other, subject only to the constraint that the total energy of subsystems A and B is constant, that is, $E_{\text{tot}} = E_A + E_B = 6$. The microstates of

E_A	accessible microstates of A		E_B	accessible microstates of subsystem B	
5	5,0	0,5	1	1,0	0, 1
	4,1	1,4			
	3,2	2,3			

Table 4.2: The 12 equally probable microstates of the isolated composite system composed of subsystems A and B with $N_A = 2$, $E_A = 5$, $N_B = 2$, and $E_B = 1$. The 12 microstates consist of all combinations of the microstates of A and B .

subsystems A and B are listed in Table 4.3 for all the possible values of E_A and E_B . The total number of microstates $\Omega_{\text{tot}}(E_A, E_B)$ accessible to the isolated composite system whose subsystems have energy E_A and E_B is

$$\Omega_{\text{tot}}(E_A, E_B) = \Omega_A(E_A)\Omega_B(E_B). \quad (4.6)$$

For example, if $E_A = 4$ and $E_B = 2$, then subsystem A can be in any one of five microstates and subsystem B can be in any of three microstates. These two sets of microstates of subsystems A and B can be combined to give $5 \times 3 = 15$ microstates of the composite system.

The total number of microstates Ω_{tot} accessible to the composite system can be found by summing $\Omega_A(E_A)\Omega_B(E_B)$ over the possible values of E_A and E_B consistent with the condition that $E_A + E_B = 6$. Hence, Ω_{tot} can be expressed as

$$\Omega_{\text{tot}} = \sum_{E_A} \Omega_A(E_A)\Omega_B(E_{\text{tot}} - E_A). \quad (4.7)$$

From Table 4.3 we see that

$$\Omega_{\text{tot}} = (7 \times 1) + (6 \times 2) + (5 \times 3) + (4 \times 4) + (3 \times 5) + (2 \times 6) + (1 \times 7) = 84. \quad (4.8)$$

Because the composite system is isolated, its accessible microstates are equally probable, that is, the composite system is equally likely to be in any one of its 84 accessible microstates. Inspection of Table 4.3 shows that the probability that the energy of the composite system is divided such that $E_A = 2$ and $E_B = 4$ is $15/84$. Let $P_A(E_A)$ be the probability that subsystem A has energy E_A . We see that $P_A(E_A)$ is given by

$$P_A(E_A) = \frac{\Omega_A(E_A)\Omega_B(E_{\text{tot}} - E_A)}{\Omega_{\text{tot}}}. \quad (4.9)$$

We show in Table 4.4 and the last column of Figure 4.3 the various values of $P_A(E_A)$.

The mean energy of subsystem A is found by calculating the ensemble average over the 84 microstates accessible to the composite system. We use the results for $P_A(E_A)$ in Table 4.4 and find that

$$\bar{E}_A = \left(0 \times \frac{7}{84}\right) + \left(1 \times \frac{12}{84}\right) + \left(2 \times \frac{15}{84}\right) + \left(3 \times \frac{16}{84}\right) + \left(4 \times \frac{15}{84}\right) + \left(5 \times \frac{12}{84}\right) + \left(6 \times \frac{7}{84}\right) = 3. \quad (4.10)$$

Problem 4.5. Standard deviation of the energy of subsystem A

Use the results of Table 4.4 to find the standard deviation of the energy of subsystem A . \square

E_A	microstates	$\Omega_A(E_A)$	E_B	microstates	$\Omega_B(E_B)$	$\Omega_A\Omega_B$	$P_A(E_A)$
6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	0	0,0	1	7	7/84
5	5,0 0,5 4,1 1,4 3,2 2,3	6	1	1,0 0,1	2	12	12/84
4	4,0 0,4 3,1 1,3 2,2	5	2	2,0 0,2 1,1	3	15	15/84
3	3,0 0,3 2,1 1,2	4	3	3,0 0,3 2,1 1,2	4	16	16/84
2	2,0 0,2 1,1	3	4	4,0 0,4 3,1 1,3 2,2	5	15	15/84
1	1,0 0,1	2	5	5,0 0,5 4,1 1,4 3,2 2,3	6	12	12/84
0	0,0	1	6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	7	7/84

Table 4.3: The 84 equally probable microstates accessible to the isolated composite system composed of subsystems A and B after the removal of the internal constraint. The total energy is $E_{\text{tot}} = E_A + E_B = 6$ with $N_A = 2$ and $N_B = 2$. Also shown are the number of accessible microstates in each subsystem and the probability $P_A(E_A)$ that subsystem A has energy E_A .

Note that the total number of microstates accessible to the isolated composite system increases from 12 to 84 when the internal constraint is removed. From the microscopic point of view, it is clear that the total number of microstates must either remain the same or increase when an internal constraint is removed. Because the number of microstates becomes a very large number for macroscopic systems, it is convenient to work with the logarithm of the number of microstates. We are thus led to define the quantity S by the relation

$$S = k \ln \Omega, \quad (4.11)$$

where k is an arbitrary constant. Note the similarity of the definition (4.11) to the expression for the missing information (3.35). We will later identify the quantity S that we have introduced in (4.11) with the thermodynamic entropy we discussed in Chapter 2.

Although our simple model has only four particles, we can ask questions that are relevant to much larger systems. For example, what is the probability that energy is transferred from one subsystem to the other? Given that $E_A = 5$ and $E_B = 1$ initially, we see from Table 4.4 that the probability of subsystem A gaining energy when the internal constraint is removed is 7/84. The

E_A	$\Omega_A(E_A)$	$\Omega_B(6 - E_A)$	$\Omega_A\Omega_B$	$P_A(E_A)$
6	7	1	7	7/84
5	6	2	12	12/84
4	5	3	15	15/84
3	4	4	16	16/84
2	3	5	15	15/84
1	2	6	12	12/84
0	1	7	7	7/84

Table 4.4: The probability $P_A(E_A)$ that subsystem A has energy E_A given that $N_A = N_B = 2$ and $E_{\text{tot}} = E_A + E_B = 6$.

probability that its energy remains unchanged is 12/84. In the remaining 65/84 cases, subsystem A loses energy and subsystem B gains energy. Because we know that energy spontaneously flows from a hotter body to a colder body, we can identify subsystem A as initially the hotter body and subsystem B as the cooler body. We will find that as the number of particles in the two subsystems becomes larger (and the energy per particle remains fixed), the probability that energy goes from the hotter to the colder subsystem rapidly increases.

Problem 4.6. Two Einstein solids in thermal contact

Consider two Einstein solids with $N_A = 4$ and $E_A = 10$ and $N_B = 4$ and $E_B = 2$. The two subsystems are thermally isolated from one another. Verify that the number of microstates accessible to subsystem A is 286 and the number of microstates accessible to subsystem B is 10. What is the initial number of accessible microstates for the composite system? The program `EinsteinSolids` determines the number of accessible microstates of an Einstein solid using (4.3) and will help you answer the following questions.

- The internal constraint is removed so that the two subsystems may exchange energy. Determine the probability $P_A(E_A)$ that system A has energy E_A . Plot P_A versus E_A and discuss its qualitative energy dependence.
- What is the probability that energy is transferred from system A to system B and from system B to system A? What is the probability that energy goes from the hotter to the colder system? How does this probability compare to the probability found from Table 4.3 for a smaller system? Which system was hotter initially?
- What is the number of accessible microstates for the composite system after the internal constraint has been relaxed? What is the change in the total entropy of the system (choose units such that $k = 1$)?
- Determine the mean energy \bar{E}_A , the most probable energy \tilde{E}_A , the standard deviations σ_A and σ_B , and the relative fluctuations σ_A/\bar{E}_A . How does the value of this ratio compare with the value of the ratio calculated in Table 4.3?
- The entropy of the composite system when each subsystem is in its most probable macrostate is $\ln \Omega_A(\tilde{E}_A)\Omega_B(E_{\text{tot}} - \tilde{E}_A)$. Compare the value of this contribution to the value of the total entropy, $\sum_{E_A} \ln \Omega_A(E_A)\Omega_B(E_{\text{tot}} - E_A)$, calculated in part (c)?

- (f) *Consider successively larger systems and describe the qualitative behavior of the various quantities. \square

From the examples and problems we have considered we conclude that it is plausible to identify thermal equilibrium with the most probable macrostate and the entropy with the logarithm of the number of accessible microstates. We also found that the probability $P(E)$ that a system has energy E is approximately a Gaussian if it can exchange energy with another system. What quantity can we identify with the temperature?

Let's return to the exchange of energy between two simple subsystems and consider the energy dependence of the entropy of each subsystem. Consider an isolated composite system consisting of two subsystems with $N_A = 3$, $N_B = 4$, and total energy $E_{\text{tot}} = 10$. The number of microstates for the two subsystems for the various possible values of E_A are summarized in Table 4.5. The most probable macrostate corresponds to $\tilde{E}_A = 4$ and $\tilde{E}_B = 6$. Because of our association of the most probable macrostate with thermal equilibrium, we know that the quantity that is the same for the two subsystems is the temperature. From our considerations in Section 2.13 we tentatively identify the inverse temperature with the derivative of the logarithm of the number of microstates of a system. In columns 5 and 10 of Table 4.5 we show the inverse slope of the entropy $S_A(E_A)$ and $S_B(E_B)$ of subsystems A and B calculated from the central difference approximation for the slopes at E_A and E_B , that is,

$$\frac{1}{T(E)} \approx \frac{[S(E + \Delta E) - S(E - \Delta E)]}{2\Delta E}. \quad (4.12)$$

(We have chosen units such that Boltzmann's constant $k = 1$.) We see from Table 4.5 that the inverse slopes of $S_A(E_A)$ and $S_B(E_B)$ are approximately equal at $E_A = \tilde{E}_A = 4$, corresponding to the value of the most probable energy. (For this small system the entropy of the composite system is not a continuous function of E_A , and thus we do not expect the slopes to be precisely equal.) We conclude that our tentative association of the temperature with the inverse slope of the entropy is plausible.

To obtain more insight into how temperature is related to the slope of the entropy, consider an energy away from equilibrium, say $E_A = 2$. Note that the slope 0.60 of $S_A(E_A = 2)$ in Table 4.5 is larger than the slope 0.30 of $S_B(E_B = 8)$. Hence, if energy is transferred from B to A , the entropy gained by A ($\Delta S = (\partial S/\partial E)\Delta E$) will be greater than the entropy lost by B , and the total entropy would increase as we expect. Because we know that energy is spontaneously transferred from "hot" to "cold," a larger slope must correspond to a lower temperature. This reasoning again suggests that the temperature is associated with the inverse slope of the energy dependence of the entropy.

Problem 4.7. More on two Einstein solids in thermal contact

Program `EntropyEinsteinSolid` computes the entropies of two Einstein solids in thermal contact.

- (a) Explore the effect of increasing the values of N_A , N_B , and the total energy E_{tot} . Discuss the qualitative dependence of S_A , S_B , and S_{tot} on the energy E_A . In particular, explain why S_A is an increasing function of E_A and S_B is a decreasing function of E_A . Given this dependence of S_A and S_B on E_A , why does S_{tot} have a maximum at a particular value of E_A ?

E_A	$\Omega_A(E_A)$	$\ln \Omega_A(E_A)$	T_A^{-1}	T_A	E_B	$\Omega_B(E_B)$	$\ln \Omega_B(E_B)$	T_B^{-1}	T_B	$\Omega_A \Omega_B$
10	66	4.19	na	na	0	1	0	na	na	66
9	55	4.01	0.19	5.22	1	4	1.39	1.15	0.87	220
8	45	3.81	0.21	4.72	2	10	2.30	0.80	1.24	450
7	36	3.58	0.24	4.20	3	20	3.00	0.63	1.60	720
6	28	3.33	0.27	3.71	4	35	3.56	0.51	1.94	980
5	21	3.05	0.31	3.20	5	56	4.03	0.44	2.28	1176
4	15	2.71	0.37	2.70	6	84	4.43	0.38	2.60	1260
3	10	2.30	0.46	2.18	7	120	4.79	0.34	2.96	1200
2	6	1.79	0.60	1.66	8	165	5.11	0.30	3.30	990
1	3	1.10	0.90	1.11	9	220	5.39	0.28	3.64	660
0	1	0	na	na	10	286	5.66	na	na	286

Table 4.5: The number of microstates of subsystems A and B for total energy $E_{\text{tot}} = E_A + E_B = 10$ and $N_A = 3$ and $N_B = 4$. The number of states was determined using (4.3). There are a total of 8008 microstates. The most probable energy of subsystem A is $\tilde{E}_A = 4$ and the fraction of microstates associated with the most probable macrostate is $1260/8008 \approx 0.157$. This fraction will approach one as the number of particles in the systems become larger.

- (b) The values of the magnitudes of the inverse slopes dS_A/dE_A and dS_B/dE_B can be obtained by clicking on the corresponding curves. The values of the magnitudes of the inverse slopes are given in the lower right corner. What is the relation of these slopes to the temperature? Determine the value of E_A at which the slopes are equal. What can you say about the total entropy at this value of E_A ? Consider a number of different values for N_A , N_B and E_{tot} . Be sure to include a case where $N_A \neq N_B$. \square

We will formally develop the relations between the number of accessible microstates of an isolated system to various quantities including the entropy and the temperature in Section 4.5.

Boltzmann probability distribution. We next consider the Einstein solid in another physical context. Consider an isolated Einstein solid of six particles with total energy $E_{\text{tot}} = 12$. We focus our attention on one of the particles and consider it as subsystem A ; subsystem B consists of the other five particles. This example is similar to the ones we have considered, but in this case subsystem A consists of only one particle. The quantity of interest is the mean energy of subsystem A , and the probability P_n that the subsystem is in microstate n with energy ϵ_n . Note that for a system of one particle the symbol n refers to the quantum number of the particle and hence its energy. The number of ways that subsystem A can be in microstate n is one because it consists of only one particle. Thus, for this special subsystem of one particle, there is a one-to-one correspondence between the microstate of the system and the energy of the system.

The number of accessible microstates of the composite system is shown in Table 4.6 using the relation (4.3). The probability P_n that the subsystem is in microstate n is plotted in Figure 4.3. Note that P_n decreases monotonically with increasing energy. A visual inspection of the energy dependence of P_n in Figure 4.3 indicates that P_n can be approximated by an exponential,

$$P_n \propto e^{-\beta \epsilon_n}, \quad (4.13)$$

microstate n	ϵ_n	$E_{\text{tot}} - \epsilon_n$	Ω_B	$P_n(\epsilon_n)$
12	12	0	$4!/(0!4!) = 1$	0.00016
11	11	1	$5!/(1!4!) = 5$	0.00081
10	10	2	$6!/(2!4!) = 15$	0.00242
9	9	3	$7!/(3!4!) = 35$	0.00566
8	8	4	$8!/(4!4!) = 70$	0.01131
7	7	5	$9!/(5!4!) = 126$	0.02036
6	6	6	$10!/(6!4!) = 210$	0.03394
5	5	7	$11!/(7!4!) = 330$	0.05333
4	4	8	$12!/(8!4!) = 495$	0.07999
3	3	9	$13!/(9!4!) = 715$	0.11555
2	2	10	$14!/(10!4!) = 1001$	0.16176
1	1	11	$15!/(11!4!) = 1365$	0.22059
0	0	12	$16!/(12!4!) = 1820$	0.29412

Table 4.6: The number of microstates accessible to subsystem A consisting of one particle. Subsystem A is in microstate n with energy $\epsilon_n = n$ and can exchange energy with subsystem B consisting of five particles. The third column is the energy of subsystem B . The total energy of the composite system is $E_{\text{tot}} = 12$. The total number of microstates is 6188, and thus $P_n = (1 \times \Omega_B)/6188$.

where $\epsilon_n = n$ in this example. The plot of $\ln P_n$ versus ϵ_n deviates from an exponential because there is a significant probability that the subsystem has a finite fraction of the total energy for this small composite system. If the number of particles in the composite system is sufficiently large so that the probability of the subsystem having a significant fraction of the total energy is negligible, then the exponential behavior of P_n becomes very well defined. These results are generalized in Section 4.6 where it is shown that the exponential decrease of the probability P_n holds exactly for a system that can exchange energy with a much larger system and that the parameter β is proportional to the inverse temperature of the much larger system. The exponential form of P_n in (4.13) is called the Boltzmann distribution.

Note that the probability P_n is usually not the same as $P(E)$. In (4.13) they are the same because there is only one particle in the subsystem, and thus there is only one way for the subsystem to have energy ϵ_n . If the subsystem has more than one particle, then there are many ways for the particles in the subsystem to share the energy (see Table 4.5). Here $P(E)$ for subsystem A is given by the probability of the subsystem being in a particular microstate with energy E multiplied by the number of microstates $\Omega_A(E)$ with the same energy E . The probability $P(E)$ is proportional to the last column in Table 4.5, which is not a Boltzmann distribution and would approach a Gaussian distribution in the limit of a large number of oscillators.

Problem 4.8. More on Einstein solids

Use the `EinsteinSolids` program to count the number of microstates for two Einstein solids that can exchange energy with one another. In this problem we wish to determine the probability $P(E_A)$ that subsystem A has energy E_A given that the total energy is $E = E_A + E_B$, and the total number of particles is N_A and N_B . The initial distribution of the energy in the program is not relevant for this problem.

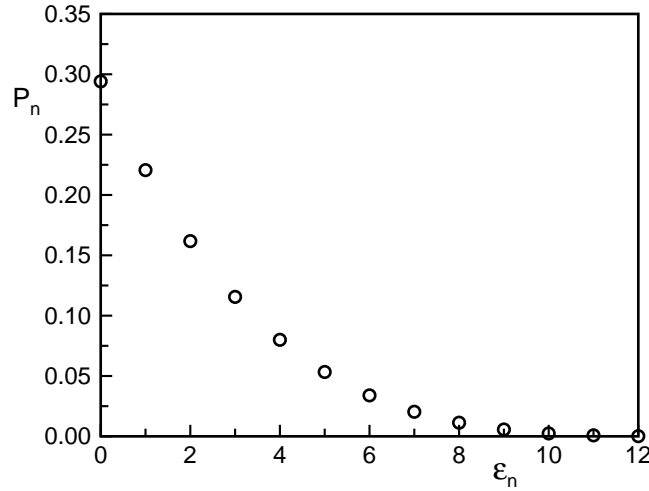


Figure 4.3: The probability P_n for the subsystem to be in microstate n with energy $\epsilon_n = n$. The subsystem can exchange energy with a system of $N = 5$ particles. The total energy of the composite system of six particles is $E_{\text{tot}} = 12$. The circles are the values of P_n given in Table 4.6.

- Choose $E = 200$ and $N_A = N_B = 4$ and estimate the width of $P_A(E_A)$. (Estimate the width at half the maximum value of $P_A(E_A)$.) Repeat for $N_A = N_B = 16$ and $N_A = N_B = 64$. How does the width depend on the number of particles? For example, does the width decrease linearly or by some other power of the number of particles?
- Repeat part (a) but with $E = 20$. Do you obtain the same dependence of the width on the number of particles. If not, why not?
- Consider $E = 200$, $N_A = 1$ and $N_B = 15$. What is the nature of $P(E_A)$? Explain why the curve is a decreasing function of E_A . \square

Problem 4.9. Qualitative behavior of the probabilities

- In Table 4.3 we considered a composite Einstein solid of four particles with two particles in each subsystem. Use the results of Table 4.3 to calculate the probability that subsystem A is in a particular microstate.

Use the `EinsteinSolids` program to help answer the following questions.

- The program computes the probability $P(E_A)$ that subsystem A has energy E_A . Consider $N_A = 4$, $N_B = 12$ and $E_{\text{tot}} = 3$. Run the program and collect the data from the `Data Table` under the `Views` menu.
- Determine the probability $P_s(E_s)$ that subsystem A is in a particular microstate by dividing $P(E_A)$ by the number of microstates with energy E_A . Plot $P_s(E_s)$.

- (d) Explain why the probabilities P_s and $P(E)$ are not the same. Why is the probability $P_s(E_s)$ a monotonically decreasing function of E_s ? What is the qualitative behavior of $P(E)$? \square

Problem 4.10. Rapid increase in the number of states

- (a) Consider an Einstein solid of $N = 20$ distinguishable particles. What is the total number of accessible microstates $\Omega(E)$ for $E = 10, 10^2, 10^3, \dots$? Is $\Omega(E)$ a rapidly increasing function of E for fixed N ?
- (b) Is Ω a rapidly increasing function of N for fixed E ? \square

4.3 Counting Microstates

In the examples we have considered so far, we have seen that the most time consuming task is enumerating (counting) the number of accessible microstates for a system of fixed energy and number of particles. We now discuss how to count the number of accessible microstates for several other systems of interest.

4.3.1 Noninteracting spins

We first reconsider an isolated system of N noninteracting spins with spin $1/2$ and magnetic moment μ in an external magnetic field B . Because we can distinguish spins at different lattice sites, a particular microstate or configuration of the system is specified by giving the orientation (up or down) of each of the N spins. We want to find the total number of accessible microstates $\Omega(E, B, N)$ for particular values of E , B , and N .

We know that if n spins are parallel to B and $N - n$ spins are antiparallel to B , the energy of the system is

$$E = n(-\mu B) + (N - n)(\mu B) = -(2n - N)\mu B. \quad (4.14)$$

For a given N and B , n specifies the energy and vice versa. If we solve (4.14) for n , we find

$$n = \frac{N}{2} - \frac{E}{2\mu B}. \quad (4.15)$$

As we found in (3.86), the total number of microstates with energy E is given by the number of ways n spins out of N can be up. This number is given by

$$\Omega(n, N) = \frac{N!}{n!(N - n)!}, \quad (4.16)$$

where n is related to E by (4.15). We will apply this result in Example 4.1 on page 198.

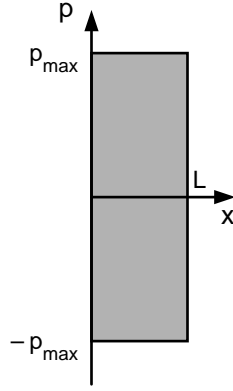


Figure 4.4: The phase space of a single particle of mass m with energy less than or equal to E in a one-dimensional box of length L . The maximum value of the momentum is $p_{\max} = \sqrt{2mE}$. Any point within the shaded rectangle corresponds to a microstate with energy less than or equal to E .

4.3.2 A particle in a one-dimensional box

Classical calculation. Consider the microstates of a single classical particle of mass m confined to a one-dimensional box of length L . We know that the microstate of a particle is specified by its position x and momentum p .² We say that the microstate (x, p) is a point in *phase space* (see Figure 4.4).

Because the values of the position and momenta of a particle are continuous variables, the number of microstates of the system with energy E is not meaningful and instead we will determine the quantity $g(E)\Delta E$, the number of microstates between E and $E + \Delta E$; the quantity $g(E)$ is the *density of states*. However, it is easier to first calculate $\Gamma(E)$, the number of microstates of the system with energy less than or equal to E (see Table 4.7). The number of microstates between E and $E + \Delta E$, $g(E)\Delta E$, is related to $\Gamma(E)$ by

$$g(E)\Delta E = \Gamma(E + \Delta E) - \Gamma(E) \approx \frac{d\Gamma(E)}{dE} \Delta E. \quad (4.17)$$

If the energy of the particle is E and the dimension of the box is L , then the microstates of the particle with energy less than or equal to E are restricted to the rectangle shown in Figure 4.4, where $p_{\max} = \sqrt{2mE}$. Because the possible values of x and p are continuous, there are an infinite number of microstates within the rectangle. As we discussed in Section 3.6, we have to group or bin the microstates so that we can count them, and hence we divide the rectangle in Figure 4.4 into bins or cells of area $\Delta x \Delta p$.

The area of the phase space occupied by the trajectory of a particle whose position x is less than or equal to L and whose energy is less than or equal to E is equal to $2p_{\max}L$. Hence, the number of cells or microstates equals

$$\Gamma_{\text{cl}}(E) = \frac{2p_{\max}L}{\Delta x \Delta p} = 2 \frac{L}{\Delta x \Delta p} (2mE)^{1/2}. \quad (4.18)$$

²We could equally well specify the velocity v rather than p , but the momentum p is the appropriate conjugate variable to x in the Hamiltonian formulation of classical mechanics.

$\Omega(E)$	Number of microstates with energy E .
$\Gamma(E)$	Number of microstates with energy less than or equal to E .
$g(E)\Delta E$	Number of microstates between E and $E + \Delta E$.
$g(E)$	Density of states.

Table 4.7: Summary of the functions used to count microstates.

In classical physics there is no criterion for choosing the values of Δx and Δp . What is the corresponding density of states?

Quantum calculation. The most fundamental description of matter at the microscopic level is given by quantum mechanics. Although the quantum mechanical description is more abstract, we will find that it makes counting microstates more straightforward (in principle).

As before, we consider a single particle of mass m in a one-dimensional box of length L . According to de Broglie, a particle has wave properties associated with it, and the corresponding standing wave has a node at the boundaries of the box. The standing wave with one antinode can be represented as in Figure 4.5; the corresponding wavelength is given by

$$\lambda = 2L. \quad (4.19)$$

The greater the number of antinodes of the wave, the greater the energy associated with the particle. The possible wavelengths that are consistent with the boundary conditions at $x = 0$ and $x = L$ satisfy

$$\lambda_n = \frac{2L}{n}, \quad (n = 1, 2, 3, \dots) \quad (4.20)$$

where the index n labels the quantum state of the particle and can be any nonzero, positive integer. From the de Broglie relation,

$$p = \frac{h}{\lambda}, \quad (4.21)$$

and the nonrelativistic relation between the energy E and the momentum p , $E = p^2/2m$, we find that the energy eigenvalues of a particle in a one-dimensional box are given by

$$E_n = \frac{p_n^2}{2m} = \frac{h^2}{2m \lambda_n^2} = \frac{n^2 h^2}{8mL^2}. \quad (4.22)$$

It is straightforward to count the number of microstates with energy less than or equal to E by solving (4.22) for n :

$$n = \frac{2L}{h}(2mE)^{1/2}. \quad (4.23)$$

Because successive microstates correspond to values of n that differ by one, the number of states with energy less than or equal to E is given by

$$\Gamma_{\text{qm}}(E) = n = \frac{2L}{h}(2mE)^{1/2}. \quad (4.24)$$

Unlike the classical case, the number of states $\Gamma_{\text{qm}}(E)$ for a quantum particle in a one-dimensional box has no arbitrary parameters such as Δx and Δp . If we require that the classical

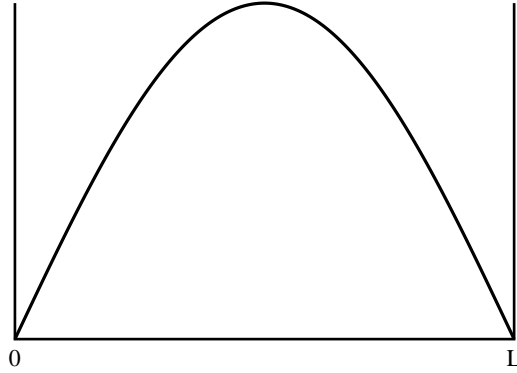


Figure 4.5: Representation of the minimum energy standing wave for a particle in a one-dimensional box. Note that the standing wave equals zero at $x = 0$ and $x = L$.

and quantum enumeration of microstates agree in the semiclassical limit,³ we see that the number of microstates, $\Gamma_{\text{cl}}(E)$ and $\Gamma_{\text{qm}}(E)$, agrees for all E if we let $2/(\Delta x \Delta p) = 1/(\pi \hbar)$. This requirement implies that the area $\Delta x \Delta p$ of a cell in phase space is given by

$$\Delta x \Delta p = h. \quad (4.25)$$

We see that Planck's constant h can be interpreted as the minimum area of a cell in a two-dimensional phase space. That is, in order for the counting of microstates in a classical system to be consistent with the more fundamental counting of microstates in a quantum system, we cannot specify a microstate of the classical system more precisely than to assign it to a cell of area h in phase space. This fundamental limitation implies that the subdivision of phase space into cells of area less than h is physically meaningless, a result consistent with the Heisenberg uncertainty principle.

It will be convenient to introduce the wave number k by the relation $k = 2\pi/\lambda$. Then we can rewrite the de Broglie relation (4.21) as

$$p = \hbar k. \quad (4.26)$$

For a particle in a one-dimensional box, we can express the condition (4.20) for a standing wave as

$$k = \frac{\pi}{L} n. \quad (n = 1, 2, 3, \dots) \quad (4.27)$$

Problem 4.11. Suppose that the energy of an electron in a one-dimensional box of length L is $E = 144 (h^2/8mL^2)$. How many microstates are there with energy less than or equal to this value of E ? \square

4.3.3 One-dimensional harmonic oscillator

The one-dimensional harmonic oscillator provides another example for which we can straightforwardly count the number of microstates in both the classical and quantum cases. The total energy

³Note that the semiclassical limit is not equivalent to simply letting $\hbar \rightarrow 0$.

of the harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2, \quad (4.28)$$

where κ is the spring constant and m is the mass of the particle.

Classical calculation. The part of phase space traversed by the trajectory $x(t), p(t)$ can be determined from (4.28) by dividing both sides by E and substituting $\omega^2 = \kappa/m$:

$$\frac{x(t)^2}{2E/m\omega^2} + \frac{p(t)^2}{2mE} = 1. \quad (4.29)$$

where the total energy E is a constant of the motion. From the form of (4.29) we see that the shape of phase space of a one-dimensional harmonic oscillator is an ellipse,

$$\frac{x^2}{a^2} + \frac{p^2}{b^2} = 1, \quad (4.30)$$

with $a^2 = 2E/(m\omega^2)$ and $b^2 = 2mE$. Hence, the area of phase space with energy less than or equal to E is $\pi ab = 2\pi E/\omega$, and the number of states in this region is

$$\Gamma_{\text{cl}}(E) = \frac{\pi ab}{\Delta x \Delta p} = \frac{2\pi E}{\omega \Delta x \Delta p}. \quad (4.31)$$

Quantum mechanical calculation. The energy eigenvalues of the harmonic oscillator are given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega. \quad (n = 0, 1, 2, \dots) \quad (4.32)$$

Because n changes by one, the number of microstates is given by

$$\Gamma_{\text{qm}}(E) = n = \frac{E}{\hbar\omega} - \frac{1}{2} \rightarrow \frac{E}{\hbar\omega}. \quad (4.33)$$

The constant $1/2$ can be neglected in the limit $E \gg \hbar\omega$. We see that $\Gamma_{\text{qm}}(E) = \Gamma_{\text{cl}}(E)$ for all E , if $2\pi/(\Delta x \Delta p) = \hbar$ or $\Delta x \Delta p = h$ as before.

4.3.4 One particle in a two-dimensional box

Consider a single particle of mass m in a rectangular box of sides L_x and L_y . The energy of the particle is given by

$$E = \frac{1}{2m}(p_x^2 + p_y^2). \quad (4.34)$$

In two dimensions the wave number becomes a wave vector \mathbf{k} , which satisfies the one-dimensional condition in each direction (see (4.27))

$$k_x = \frac{\pi}{L_x}n_x, \quad k_y = \frac{\pi}{L_y}n_y. \quad (n_x, n_y = 1, 2, 3, \dots) \quad (4.35)$$

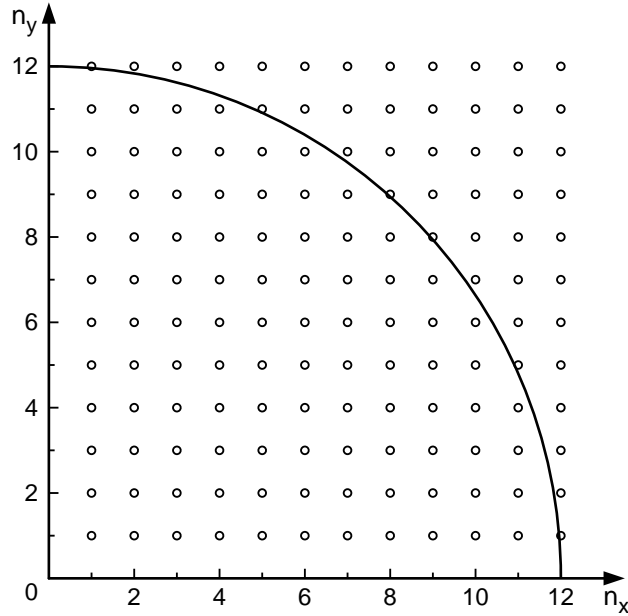


Figure 4.6: The points represent possible values of n_x and n_y such that $R^2 = n_x^2 + n_y^2 = 12^2$. Note that n_x and n_y are integers with $n_x, n_y \geq 1$. Each point represents a single particle microstate. What is the total number of states for $R = 12$? The corresponding number from the asymptotic relation is $\Gamma(E) = \pi 12^2/4 \approx 113$.

The corresponding eigenvalues are given by

$$E_{n_x, n_y} = \frac{h^2}{8m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right]. \quad (4.36)$$

The states of the particle are labeled by the two integers n_x and n_y with $n_x, n_y \geq 1$. The area associated with each single particle state in the space defined by the points (n_x, n_y) is one as can be seen in Figure 4.6. For simplicity, we assume that $L_x = L_y \equiv L$. The values of (n_x, n_y) for a given E satisfy the condition

$$R^2 = n_x^2 + n_y^2 = \left(\frac{2L}{h} \right)^2 (2mE). \quad (4.37)$$

For large values of n_x and n_y the values of n_x and n_y that correspond to states with energy less than or equal to E lie inside the positive quadrant of a circle of radius R , where

$$R = \frac{2L}{h} (2mE)^{1/2}. \quad (4.38)$$

Hence, the number of states with energy less than or equal to E is given by

$$\Gamma(E) = \frac{1}{4} \pi R^2 = \pi \frac{L^2}{h^2} (2mE). \quad (4.39)$$

Note that $V = L^2$ in this case.

Problem 4.12. Finite size effects in two dimensions

The expression (4.39) for $\Gamma(E)$ is valid only for large E because the area of a quadrant of a circle overestimates the number of lattice points n_x, n_y inside a circle of radius R . Use the `IdealGasNumberOfStates` program to explore how the relation $\Gamma = \pi R^2/4$ approximates the actual number of microstates. The program computes the number of nonzero, positive integers that satisfy the condition $n_x^2 + n_y^2 \leq R^2$. What is the minimum value of R for which the difference between the asymptotic relation and the exact number is less than 1%? \square

4.3.5 One particle in a three-dimensional box

The generalization to three dimensions is straightforward. If we assume that the box is a cube with linear dimension L , we have

$$E = \frac{h^2}{8mL^2}[n_x^2 + n_y^2 + n_z^2]. \quad (4.40)$$

The values of n_x , n_y , and n_z that correspond to microstates with energy less than or equal to E lie inside the positive octant of a sphere of radius R given by

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \left(\frac{2L}{h}\right)^2 (2mE). \quad (4.41)$$

Hence

$$\Gamma(E) = \frac{1}{8} \left(\frac{4}{3}\pi R^3\right) = \frac{\pi}{6} \left(\frac{2L}{h}\right)^3 (2mE)^{3/2} = \frac{4\pi}{3} \frac{V}{h^3} (2mE)^{3/2}, \quad (4.42)$$

where we have let $V = L^3$.

Problem 4.13. Finite size effects in three dimensions

The expression (4.42) for $\Gamma(E)$ is valid only for large E because the area of an octant of a sphere overestimates the number of lattice points n_x, n_y, n_z . Use the `IdealGasNumberOfStates` program to determine how the relation $\Gamma = \pi R^3/6$ approximates the total number of microstates, as in Problem 4.12. \square

Problem 4.14. Estimation of the number of states

Estimate the number of microstates accessible to a gas molecule in a one liter box at room temperature. The mean energy E of a gas molecule such as nitrogen at room temperature can be found from the relation $E = 3kT/2$. Consider an energy interval $\Delta E = 10^{-27}$ J that is much smaller than E , and calculate the number of microstates $g(E)\Delta E$ accessible to the molecule in the interval between E and $E + \Delta E$. Refer to (4.42) and (4.17). \square

4.3.6 Two noninteracting identical particles and the semiclassical limit

Consider two noninteracting particles of mass m of the same species in a one-dimensional box of length L . The total energy is given by

$$E_{n_1, n_2} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2), \quad (4.43)$$

where the quantum numbers n_1 and n_2 are positive nonzero integers. To count the microstates correctly, we need to take into account that particles of the same species are *indistinguishable*, one of the fundamental principles of quantum mechanics.

As an example of how to count the microstates of this two particle system, suppose that each particle can be in one of the four lowest single particle energy states. The values of n_1 and n_2 that satisfy this constraint are given in Table 4.8. The indistinguishability of the particles means that we cannot assign the quantum numbers n_1 independently n_2 . For example, because the state $(n_1 = 1, n_2 = 2)$ is indistinguishable from the state $(n_1 = 2, n_2 = 1)$, we can include only one of these states.

The assignment of quantum numbers is further complicated by the fact that the particles must obey quantum statistics. We will discuss the nature of quantum statistics in Section 6.3. In brief, particles must obey either Bose or Fermi statistics. If the particles obey Bose statistics, then any number of particles may be in the same single particle quantum state. In contrast, if the particles obey Fermi statistics, then two particles may not be in the same single particle quantum state, and hence the states $(n_1, n_2) = (1, 1), (2, 2), (3, 3)$ and $(4, 4)$ are excluded.

distinguishable particles		Bose statistics		Fermi statistics	
n_1	n_2	n_1	n_2	n_1	n_2
1	1	1	1		
2	1	2	1	2	1
1	2				
2	2	2	2		
3	1	3	1	3	1
1	3				
3	2	3	2	3	2
2	3				
3	3	3	3		
4	1	4	1	4	1
1	4				
4	2	4	2	4	2
2	4				
4	3	4	3	4	3
3	4				
4	4	4	4		

Table 4.8: The microstates of two identical noninteracting particles of mass m in a one-dimensional box such that each particle can be in one of the four lowest energy states. The rows are ordered by their total energy. If the particles obey Fermi statistics, they cannot be in the same microstate, so $n_1 = 1, n_2 = 1$ is not allowed. There is no such restriction for Bose statistics. Because the particles are identical and hence indistinguishable quantum mechanically, $n_1 = 1, n_2 = 2$ and $n_1 = 2, n_2 = 1$ are the same microstate.

Because the particles are indistinguishable, there are fewer microstates than if the particles were distinguishable, and we might think that enumerating the accessible microstates is easier. However, it is much more difficult because we cannot enumerate the states for each particle indi-

vidually even though the particles do not interact. For example, if $n_1 = 1$, then $n_2 \neq 1$ for Fermi statistics. However, the counting of microstates can be simplified in the *semiclassical limit*. In this limit the number of single particle states is much greater than the number of particles. (Obviously, that is not the case in our simple example where each particle is limited to four states.) In the semiclassical limit we do not care if two particles are put in the same single particle state because there will be many more states where this counting error (for fermions) does not occur. Hence we can assign states to one particle separately without regard to the state of the other particle.

In our example there is a maximum of $4 \times 4 = 16$ possible states because particles 1 and 2 can each be in one of four states. Because the particles are indistinguishable and a state such as $n_1 = 3, n_2 = 4$ cannot be distinguished from $n_1 = 4, n_2 = 3$, we divide by $2!$ to approximately correct for overcounting. This correction gives $(4 \times 4)/2! = 8$ states. The actual number for Bose statistics is 10 and Fermi statistics is 6. Dividing by $2!$ is not a good approximation for such a small system. However, if the number of possible states Γ for each particle is much greater than the number of particles N , then dividing by $N!$ is a very good approximation. To understand the nature of this approximation lets consider the equivalent problem of the number of ways of putting N identical balls into Γ boxes. This number is given by

$$\frac{(N + \Gamma - 1)!}{N!(\Gamma - 1)!} \quad (4.44)$$

Equation (4.44) is the same expression we used for counting the number of identical quanta of energy that can be distributed among distinct oscillators in the Einstein model. Note that (4.44) counts all the ways of placing the balls into boxes, including putting more than one ball into a box. You can test (4.44) by working out a simple example. In (4.44) the last $\Gamma - 1$ factors in the numerator are canceled by $(\Gamma - 1)!$ in the denominator, and we are left with N more factors, each of which are approximately equal to Γ if $\Gamma \gg N$. Thus, to convert the number of ways of assigning N distinguishable particles (Γ^N) to the number of ways of assigning N indistinguishable particles, we need to divide Γ^N by $N!$. Another way of obtaining this result is to assume that N of the boxes have been filled with one ball each. There is only way to do so if the balls are identical. If the balls are distinguishable, there are N different balls that can occupy box 1, which leaves $N - 1$ different balls that can occupy box 2, $N - 2$ balls that can occupy box 3, and so on, which leads to the factor of $N!$. Because $\Gamma \gg N$, the probability of multiple occupancy of any state is negligible and, thus there is no distinction between Bose and Fermi systems in the semiclassical limit.

4.4 The Number of States of Many Noninteracting Particles: Semiclassical Limit

We now apply these considerations to determine the number of microstates of an ideal classical gas of N particles in a three-dimensional box in the semiclassical limit. (A simpler way to do so that yields the correct E and V dependence is given in Problem 4.15, but the numerical factors are not identical to the result of the more accurate calculation that we discuss here.)

The idea is to first count the microstates assuming that the N particles are distinguishable and then divide by $N!$ to correct for the overcounting. We know that for one particle in a three-dimensional box the number of microstates with energy less than or equal to E is given by the volume of the positive part (or octant) of the three-dimensional sphere of radius $R = (2L/h)(2mE)^{1/2}$

(see (4.38)). For N distinguishable particles in a three-dimensional box, the number of microstates with energy less than or equal to E is given by the volume of the positive part of a $3N$ -dimensional hypersphere of radius $R = (2L/h)(2mE)^{1/2}$. In Section 4.14.1 we write the volume $V_n(R)$ of a n -dimensional hypersphere of radius R as

$$V_n(R) = \int_{x_1^2 + x_2^2 + \dots + x_n^2 < R^2} dx_1 dx_2 \dots dx_n. \quad (4.45)$$

where x_i is the position coordinate in the i th direction. For example, in three dimensions (x_1, x_2, x_3) represents the usual coordinates (x, y, z) . The volume $V_n(R)$ is given by (see Section 4.14.1)

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n, \quad (\text{integer } n) \quad (4.46)$$

where the Gamma function satisfies the relations $\Gamma(n+1) = n\Gamma(n)$, $\Gamma(1/2) = \sqrt{\pi}$. For integer n $\Gamma(n) = (n-1)!$, and the Gamma function can be interpreted as a generalization of the factorial. The cases $n = 2$ and $n = 3$ yield the expected results, $V_2 = 2\pi R^2/(2\Gamma(1)) = \pi R^2$ because $\Gamma(1) = 1$, and $V_3 = 2\pi^{3/2} R^3/(3\Gamma(3/2)) = 4\pi R^3/3$ because $\Gamma(3/2) = \Gamma(1/2)/2 = \sqrt{\pi}/2$. The volume of the positive part of the n -dimensional sphere of radius R is given by⁴

$$\Gamma_n(R) = \left(\frac{1}{2}\right)^n V_n(R). \quad (4.47)$$

We are interested in the case $n = 3N$ and $R = (2mE)^{1/2}(2L/h)$. In this case the volume $\Gamma(E, V, N)$ is given by

$$\Gamma(E, V, N) = \left(\frac{1}{2}\right)^{3N} \frac{2\pi^{3N/2}}{3N(3N/2-1)!} R^{3N/2} \quad (4.48a)$$

$$= \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} R^{3N/2} \quad (4.48b)$$

$$= \left(\frac{1}{2}\right)^{3N} \left(\frac{2L}{h}\right)^{3N/2} \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} \quad (4.48c)$$

$$= \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \quad (4.48d)$$

If we include the factor of $1/N!$ to correct for the overcounting of microstates in the semiclassical limit, we obtain the desired result:

$$\Gamma(E, V, N) = \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \quad (\text{semiclassical limit}) \quad (4.49)$$

$\Gamma(E, V, N)$ is the number of states of N noninteracting particles in a three-dimensional box of volume V in the semiclassical limit.

⁴The volume $\Gamma_n(R)$ should not be confused with the Gamma function $\Gamma(n)$.

A more convenient expression for $\Gamma(E, V, N)$ can be found by using Stirling's approximation (3.101) for $N \gg 1$. We have

$$\ln \Gamma(E, V, N) = -\ln N! + N \ln \frac{V}{h^3} + \frac{3}{2}N \ln(2\pi mE) - \ln \left(\frac{3N}{2} \right)! \quad (4.50a)$$

$$\approx -N \ln N + N + N \ln V - \frac{3N}{2} \ln h^2 + \frac{3}{2}N \ln(2\pi mE) - \frac{3}{2}N \ln \frac{3N}{2} + \frac{3N}{2} \quad (4.50b)$$

$$= N \ln \frac{V}{N} + \frac{3}{2}N \ln \frac{4\pi mE}{3N h^2} + \frac{5}{2}N. \quad (4.50c)$$

It is frequently convenient to write $\ln \Gamma(E, V, N)$ in terms of \hbar instead of h :

$$\ln \Gamma(E, V, N) = N \ln \frac{V}{N} + \frac{3}{2}N \ln \frac{mE}{3N\pi\hbar^2} + \frac{5}{2}N. \quad (4.51)$$

Problem 4.15. Approximate expression for $\Gamma(E, V, N)$

We can obtain an approximate expression for $\Gamma(E, V, N)$ using simpler physical considerations. We write

$$\Gamma(E, V, N) \approx \frac{1}{N!} \Gamma_1 \left(\frac{E}{N}, V \right) \Gamma_1 \left(\frac{E}{N}, V \right) \dots \Gamma_1 \left(\frac{E}{N}, V \right) = \frac{1}{N!} \Gamma_1 \left(\frac{E}{N}, V \right)^N, \quad (4.52)$$

where $\Gamma_1(E, V)$ is the number of states of a single particle with energy less than E in a three-dimensional box of volume V . We have assumed that on the average each particle has an energy E/N . Find the form of $\Gamma(E, V, N)$ using the relation (4.42) for Γ_1 . How does the dependence on V and E of $\Gamma(E, V, N)$ obtained from this simple argument compare to the V and E dependence of Ω in (4.49). What about the N -dependence? \square

Problem 4.16. Density of states of an ideal gas

Use (4.51) to calculate the density of states $g(E, V, N)$ and verify that $\Gamma(E, V, N)$ and $g(E, V, N)$ are rapidly increasing functions of E , V , and N . \square

4.5 The Microcanonical Ensemble (Fixed E, V, and N)

The macrostate of an isolated system of particles is specified by the energy E , volume V , and number of particles N of the system. All the microstates that are consistent with these conditions are assumed to be equally probable. The collection of systems in the different microstates with the specified values of E , V , and N is called the *microcanonical ensemble*. More precisely, because the energy E is a continuous variable, the energy is specified to be in the range E to $E + \Delta E$, where $\Delta E \ll E$.

In the following we show how the quantities that correspond to the usual thermodynamic quantities, for example, the entropy, temperature, and pressure, are related to the number of microstates. (It might be helpful to review the sections in Chapter 2 on the definitions of the various thermodynamic derivatives and free energies.) We will then use these relations to derive the ideal classical gas equation of state and other well known results using (4.51) for the number of microstates of an ideal gas of N particles in a volume V with energy less than or equal to E in the semiclassical limit.

We first establish the connection between the number of accessible microstates to various thermodynamic quantities by using arguments that are similar to our treatment of the simple models that we considered in Section 4.2. Consider two isolated systems A and B that are separated by an insulating, rigid, and impermeable wall. The macrostate of each system is specified by E_A, V_A, N_A and E_B, V_B, N_B , respectively, and the corresponding number of microstates is $\Omega_A(E_A, V_A, N_A)$ and $\Omega_B(E_B, V_B, N_B)$. Equilibrium in this context means that each accessible microstate is equally represented in the ensemble. The number of microstates of the composite system consisting of the two isolated subsystems A and B is

$$\Omega = \Omega_A(E_A, V_A, N_A) \Omega_B(E_B, V_B, N_B). \quad (4.53)$$

We want a definition of the entropy that is a measure of the number of microstates and that is additive for independent systems. We will assume that S is related to Ω by⁵

$$\boxed{S = k \ln \Omega}. \quad (4.54)$$

If we substitute (4.53) in (4.54), we find that $S = S_A + S_B$, and S is an additive function.

Next we modify the wall between A and B so that the wall becomes conducting, but remains rigid and impermeable. We say that we have relaxed the internal constraint of the composite system. The two subsystems are now in thermal contact so that the energies E_A and E_B can vary, subject to the condition that the total energy $E = E_A + E_B$ is fixed; the volumes V_A and V_B and particle numbers N_A and N_B remain unchanged. What happens to the number of accessible microstates after we relax the internal constraint? If subsystem A has energy E_A , it can be in any one of its $\Omega(E_A)$ microstates. Similarly, subsystem B can be in any one of its $\Omega_B(E - E_A)$ microstates. Because every possible microstate of A can be combined with every possible microstate of B to give a different microstate of the composite system, it follows that the number of microstates accessible to the composite system when A has energy E_A is the product $\Omega_A(E_A)\Omega_B(E - E_A)$. Hence, the total number of accessible microstates of the composite system is

$$\Omega(E) = \sum_{E_A} \Omega_A(E_A) \Omega_B(E - E_A). \quad (4.55)$$

The probability that system A has energy E_A is given by

$$P(E_A) = \frac{\Omega_A(E_A) \Omega_B(E - E_A)}{\Omega(E)}. \quad (4.56)$$

Note that we have implicitly assumed that the interaction between the two systems is weak so that the microstates of each system are unchanged. Because the two systems interact only at the boundary between them, the fraction of particles at the boundary goes to zero in the thermodynamic limit $N, V \rightarrow \infty, \rho = N/V = \text{constant}$. That is, the number of particles at the boundary is proportional to the surface area L^2 , and the number of particles in the bulk is proportional to the volume $V = L^3$, where L is the linear dimension of the system.

The logarithm of (4.55) does not yield a sum of two functions. However, the dominant contribution to the right-hand side of (4.55) for $N \gg 1$ comes from the term with $E_A = \tilde{E}_A$, where

⁵Equation (4.54) is a consequence of Boltzmann's work, but was first written in this form by Max Planck. The constant k is known as Boltzmann's constant but was first introduced by Planck.

\tilde{E}_A is the most probable value of E_A . With this approximation we can write

$$\Omega(E) \approx \Omega_A(\tilde{E}_A)\Omega_B(E - \tilde{E}_A). \quad (4.57)$$

The approximation (4.57) better approximates the sum in (4.55) as the thermodynamic limit is approached and allows us to write

$$S = k \ln \Omega = S_A + S_B \quad (4.58)$$

before and after the constraint is removed. We see that one consequence of the proposed relation between S and Ω is that the entropy increases or remains unchanged after an internal constraint is relaxed.

Given the definition (4.54) of S as a function of E , V , and N , it is natural to adopt the thermodynamic definitions of temperature, pressure, and chemical potential:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} \quad (4.59)$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} \quad (4.60)$$

$$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,V}. \quad (4.61)$$

The definition of the entropy $S = k \ln \Omega$ in (4.54) gives us the desired connection between statistical mechanics and thermodynamics.

How should we generalize the relation of S to the number of microstates for a system in which the energy is a continuous variable? Two possibilities are

$$S = k \ln g(E)\Delta E \quad (4.62a)$$

$$S = k \ln \Gamma(E). \quad (4.62b)$$

It is easy to show that in the limit $N \rightarrow \infty$, the two definitions yield the same result (see Problem 4.18). The reason is that $\Gamma(E)$ and $g(E)$ are such rapidly increasing functions of E that it makes no difference whether we include the microstates with energy less than or equal to E or just the states between E and $E + \Delta E$.

If we use either of the definitions of S given in (4.62) and (4.51), we find that the entropy of an ideal gas in the semiclassical limit for $N \rightarrow \infty$ is given by

$$S(E, V, N) = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{mE}{3N\pi\hbar^2} + \frac{5}{2} \right]. \quad (4.63)$$

Problem 4.17. Form of the entropy

Compare the form of S given in (4.63) with the form of S determined from thermodynamic considerations in Section 2.19. □

Problem 4.18. Equivalent definitions of the entropy

Verify the result (4.63) for the entropy S of an ideal gas using either of the definitions of S given in (4.62). Why can we neglect ΔE compared to E when we use the definition (4.62a)? □

We now use the result (4.63) for S to obtain the energy equation of state of an ideal classical gas. From (4.63) we see that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{3}{2} \frac{Nk}{E}, \quad (4.64)$$

and hence we obtain the familiar result

$$E = \frac{3}{2} NkT. \quad (4.65)$$

The pressure equation of state follows from (4.60) and (4.63) and is given by

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{Nk}{V}, \quad (4.66)$$

and hence

$$PV = NkT. \quad (4.67)$$

We have finally derived the thermal and mechanical equations of state of an ideal classical gas from first principles! Do the equations of state depend on \hbar and parameters such as m which appear in (4.49)?

Problem 4.19. The Sackur-Tetrode expression for the entropy

Use the relations (4.63) and (4.65) to obtain S as a function of T , V , and N instead of E , V , and N . This relation is known as the *Sackur-Tetrode* equation. \square

Problem 4.20. The chemical potential of an ideal gas

Use (4.61) and (4.63) to derive the dependence of the chemical potential μ on E , V , and N for an ideal classical gas. Then use (4.65) to determine $\mu(T, V, N)$. We will derive $\mu(T, V, N)$ for the ideal classical gas more simply in Section 6.6. \square

So far we have used the relation (4.54) between the entropy and the number of accessible states to find the equation of states of an ideal classical gas. In Example 4.1 we apply the same formalism to find the energy equation of state of a system of noninteracting spins.

Example 4.1. Isolated system of N spins

Consider a system of N noninteracting spins and find the dependence of its temperature T on the total energy E . What is the probability that a given spin is up?

Solution. We first have to find the dependence of the entropy S on the energy E of the system. As discussed in Sec. 4.3.1, the energy E of a system with n spins up out of N in a magnetic field B is

$$E = -(n - n')\mu B = -[n - (N - n)]\mu B = -(2n - N)\mu B, \quad (4.14)$$

where $n' = N - n$ is the number of down spins and μ is the magnetic moment of the spins. From (4.14) we find that the value of n corresponding to a given E is given by

$$n = \frac{1}{2} \left(N - \frac{E}{\mu B} \right). \quad (4.68)$$

The corresponding number of microstates is given by

$$\Omega(n) = \frac{N!}{n!(N-n)!}. \quad (4.16)$$

The thermodynamic temperature T is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{B,N} = \frac{dS(n)}{dn} \frac{dn}{dE} = -\frac{1}{2\mu B} \frac{dS}{dn}. \quad (4.69)$$

To calculate dS/dn , we use the approximation (3.104) for large n :

$$\frac{d}{dn} \ln n! = \ln n, \quad (4.70)$$

and find

$$\frac{dS(n)}{dn} = k[-\ln n + \ln(N-n)], \quad (4.71)$$

where $S(n) = k \ln \Omega(n)$ from (4.16). Hence

$$\frac{1}{T} = -k \frac{1}{2\mu B} \ln \frac{N-n}{n}. \quad (4.72)$$

Equation (4.72) yields T as a function of E by eliminating n using (4.68).

The natural variables in the microcanonical ensemble are E , V , and N . Hence, T is a derived quantity and is found as a function of E . As shown in Problem 4.21, we can use (4.14) and (4.72) to express E as a function T . The result is

$$E = -N\mu B \tanh \frac{\mu B}{kT} = -N\mu B \tanh \beta\mu B, \quad (4.73)$$

where $\beta = 1/kT$.

The probability p that a given spin is up is equal to the ratio n/N . If we solve (4.72) for n/N , we find (see Problem 4.21)

$$p = \frac{n}{N} = \frac{1}{1 + e^{-2\mu B/kT}}, \quad (4.74a)$$

$$= \frac{e^{\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} = \frac{e^{\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}. \quad (4.74b)$$

We have obtained the result for p that we promised in Section 3.5. \diamond

Note we had to consider all N spins even though the spins do not interact with each other. The reason is that the N spins have a definite energy and hence we cannot assign the orientation of each spin independently. We will obtain the result (4.74) by a more straightforward method in Section 4.6.

Problem 4.21. The energy as a function of the temperature

Solve (4.72) for n/N and verify (4.74). Then use (4.14) to solve for E as a function of T and verify (4.73) for a system of N noninteracting spins. \square

ensemble	macrostate	probability distribution	thermodynamics
microcanonical	E, V, N	$P_s = 1/\Omega$	$S(E, V, N) = k \ln \Omega$
canonical	T, V, N	$P_s = e^{-\beta E_s} / Z$	$F(T, V, N) = -kT \ln Z$
grand canonical	T, V, μ	$P_s = e^{-\beta(E_s - \mu N_s)} / Z_G$	$\Omega_G(T, V, \mu) = -kT \ln Z_G$

Table 4.9: Summary of the three most common ensembles. P_s is the probability that the system is in a particular microstate s .

Although the microcanonical ensemble is conceptually simple, it is almost always not the most practical ensemble. The major problem is that because we must satisfy the constraint that E is specified, we cannot assign energies to each particle individually, even if the particles do not interact. Also because each microstate is equally probable, there are no obvious approximation methods that retain only the most important microstates. Moreover, isolated systems are very difficult to realize experimentally, and the temperature rather than the energy is a more natural independent variable.

Before we discuss the other common ensembles, we summarize their general features in Table 4.9. The internal energy E is fixed in the microcanonical ensemble and the temperature is a derived quantity. In the canonical ensemble the temperature T and hence the mean energy is fixed, but the energy fluctuates. Similarly, the chemical potential and hence the mean number of particles is fixed in the grand canonical ensemble, and the number of particles fluctuates. In all of these ensembles, the volume V is fixed which implies that the pressure fluctuates. We also can choose an ensemble in which the pressure is fixed and the volume fluctuates.

***Problem 4.22.** The Einstein solid in the microcanonical ensemble

Consider a collection of N distinguishable harmonic oscillators with total energy E . The oscillators are distinguishable because they are localized on different lattice sites. In one dimension the energy of each particle is given by $\epsilon_n = (n + \frac{1}{2})\hbar\omega$, where ω is the angular frequency. Hence, the total energy can be written as $E = (Q + \frac{1}{2}N)\hbar\omega$, where Q is the number of quanta. Calculate the dependence of the temperature T on the total energy E in the microcanonical ensemble using the result that the number of accessible microstates in which N distinguishable oscillators can share Q indistinguishable quanta is given by $\Omega = (Q + N - 1)!/Q!(N - 1)!$ (see (4.3)). Then use this relation to find $E(T)$. This relation is calculated much more simply in the canonical ensemble as shown in Example 4.3. \square

4.6 The Canonical Ensemble (Fixed T, V, and N)

We now assume that the system of interest can exchange energy with a much larger system known as a *heat bath*. The heat bath is sufficiently large that it is not significantly affected by the smaller system. For example, if we place a glass of cold water into a large room, the temperature of the water will eventually reach the temperature of the air in the room. Because the volume of the glass is small compared to the volume of the room, the cold water does not cool the air appreciably and the air is an example of a heat bath.

The composite system, the system of interest plus the heat bath, is an isolated system. We can characterize the macrostate of the composite system by E, V, N . The accessible microstates of the composite system are equally probable. If the system of interest is in a microstate with energy E_s , then the energy of the heat bath is $E_b = E - E_s$. Because the system of interest is much smaller than the heat bath, we know that $E_s \ll E$.⁶

For a given microstate of the system, the heat bath can be in any one of a large number of microstates such that the total energy of the composite system is E . The probability P_s that the system is in microstate s with energy E_s is given by (see (4.53))

$$P_s = \frac{1 \times \Omega_b(E - E_s)}{\sum_s \Omega_b(E - E_s)}, \quad (4.75)$$

where $\Omega_b(E - E_s)$ is the number of microstates of the heat bath for a given microstate s of the system of interest. As E_s increases, $\Omega_b(E - E_s)$, the number of accessible microstates available to the heat bath, decreases. We conclude that P_s is a decreasing function of E_s , because the larger the value of E_s , the less energy is available to the heat bath.

We can simplify the form of P_s by using the fact that $E_s \ll E$. We cannot approximate $\Omega_b(E - E_s)$ directly because Ω_b is a rapidly varying function of its argument. For this reason we take the logarithm of (4.75) and write

$$\ln P_s = C + \ln \Omega_b(E_b = E - E_s), \quad (4.76)$$

where the constant C is related to the denominator of (4.75) and does not depend on E_s . We now expand $\ln \Omega_b(E - E_s)$ to leading order in E_s and write

$$\ln P_s \approx C + \ln \Omega_b(E) - E_s \left(\frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \right)_{E_b=E} \quad (4.77a)$$

$$= C + \ln \Omega_b(E) - \frac{E_s}{kT}. \quad (4.77b)$$

We have used the relations (from (4.54) and (4.59))

$$\beta \equiv \frac{1}{kT} = \left(\frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \right)_{N,V}, \quad (4.78)$$

where T is the temperature of the heat bath. As can be seen from (4.78), β is proportional to the inverse temperature of the heat bath. From (4.77b) we obtain

$$\boxed{P_s = \frac{1}{Z} e^{-\beta E_s}}. \quad (\text{Boltzmann distribution}) \quad (4.79)$$

The function Z is found from the normalization condition $\sum_s P_s = 1$ and is given by

$$\boxed{Z = \sum_s e^{-\beta E_s}}. \quad (\text{partition function}) \quad (4.80)$$

⁶It is not obvious how we should assign the potential energy of interaction of particles at the interface of the system and the heat bath. If the number of particles in the system of interest is large, the number of particles near the interface between the two systems is small in comparison to the number of particles in the bulk so that the potential energy of interaction of particles near the surface can be ignored. Nevertheless, these interactions are essential in order for the system to come into thermal equilibrium with the heat bath.

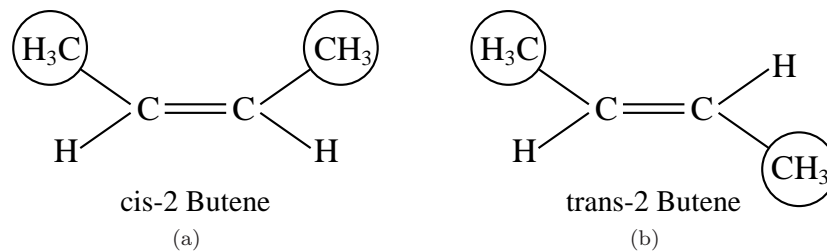


Figure 4.7: Butene (C_4H_8) is a colorless gas at room temperature and pressure. It exists in four isomers or structures, two of which are shown. The trans-2 isomer in (b) has lower energy than the cis-2 isomer in (a).

The $Z(T, V, N)$ is known as the *partition function*. The symbol Z is from the German *Zustandssumme*, which means “sum over states.” The form of P_s in (4.79) applies to a system in equilibrium with a heat bath at temperature T . Note that our derivation of the Boltzmann distribution holds for any system in equilibrium with a heat bath and makes no assumption about the nature of the system and the heat bath.

Problem 4.23. Discuss the relation between the qualitative results that we obtained based on Table 4.6 and the Boltzmann distribution in (4.79). \square

Problem 4.24. Relative abundance of two isomers

The hydrocarbon 2-butene, $\text{CH}_3\text{-CH=CH-CH}_3$ occurs in two isomers (geometrical structures) called cis and trans. The cis (on this side) isomer of 2-butene has both CH_3 groups on the same side of the $\text{C}=\text{C}$ double bond. In the trans (across) isomer the CH_3 groups are on opposite sides of the double bond (see Figure 4.7). The energy difference ΔE between the two conformations is approximately $\Delta E/k = 4180\text{K}$, with the trans isomer lower than the cis isomer. Determine the relative abundance of the two conformations at $T = 300\text{K}$ and $T = 1000\text{K}$. \square

In the canonical ensemble the temperature T is fixed by the heat bath, and a macrostate is specified by the temperature T , volume V , and the number of particles N . The mean energy of the system is given by

$$\bar{E} = \sum_s P_s E_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s}, \quad (4.81)$$

where we have substituted the Boltzmann form (4.79) for the probability distribution. We use a trick similar to that used in Section 3.5 to obtain a simpler form for \bar{E} . First we write

$$\bar{E} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s}, \quad (4.82)$$

where we have used the fact that $\frac{\partial}{\partial \beta}(e^{-\beta E_s}) = -E_s e^{-\beta E_s}$. Because

$$\frac{\partial Z}{\partial \beta} = -\sum_s E_s e^{-\beta E_s}, \quad (4.83)$$

we can write

$$\boxed{\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z.} \quad (4.84)$$

We see that \bar{E} is a function of T for fixed V and N and can be expressed as a derivative of Z .

In the same spirit we can express C_V , the heat capacity at constant volume, in terms of Z . We have

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{d\beta}{dT} \frac{\partial \bar{E}}{\partial \beta}, \quad (4.85)$$

$$= \frac{1}{kT^2} \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \right], \quad (4.86)$$

where $\partial \bar{E} / \partial \beta$ has been calculated from (4.84). Because

$$\overline{E^2} = \frac{1}{Z} \sum_s E_s^2 e^{-\beta E_s} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}, \quad (4.87)$$

we obtain the relation

$$\boxed{C_V = \frac{1}{kT^2} \left[\overline{E^2} - \bar{E}^2 \right].} \quad (4.88)$$

Equation (4.88) relates the response of the system to a change in energy to the equilibrium energy fluctuations. Note that we can calculate the variance of the energy, a measure of the magnitude of the energy fluctuations, from the heat capacity. We will later find other examples of the relation of the linear response of an equilibrium system to the equilibrium fluctuations of an associated quantity.⁷

Because the energy is restricted to a very narrow range in the microcanonical ensemble and can range anywhere between zero and infinity in the canonical ensemble, it is not obvious that the two ensembles give the same results for the thermodynamic properties of a system. One way to understand why the thermodynamic properties are independent of the choice of ensemble is to use the relation (4.88) to estimate the range of energies in the canonical ensemble that have a significant probability. Because both E and C_V are extensive quantities, they are both proportional to N . Hence, the N -dependence of the relative fluctuations of the energy in the canonical ensemble is given by

$$\frac{\sqrt{\overline{E^2} - \bar{E}^2}}{\bar{E}} = \frac{\sqrt{kT^2 C_V}}{\bar{E}} \sim \frac{N^{1/2}}{N} \sim N^{-1/2}. \quad (4.89)$$

From (4.89) we see that in the limit of large N , the relative fluctuations in the values of E that would be observed in the canonical ensemble are vanishingly small. For this reason the mean energy in the canonical ensemble is a well defined quantity just like it is in the microcanonical ensemble. However, the fluctuations in the energy are qualitatively different in the two ensembles.

⁷The relation (4.88) is important conceptually and is useful for simulations at a given temperature (see Section 4.11). However, it is almost always more convenient to *calculate* C_V from its definition in (4.85).

Problem 4.25. Distribution of energy in the canonical ensemble

Given what you have learned so far about the N -dependence of the relative energy fluctuations, what is your best guess for the form of the probability that a system in equilibrium with a heat bath at temperature T has energy between E and $E + \Delta E$? The form of the probability distribution of the energy of a system in the canonical ensemble is derived in Section 4.14.2. \square

Problem 4.26. The Boltzmann probability given by (4.79) is the probability that the system is in a particular microstate with energy E_s . On the basis of what you have learned so far, what do you think is the form of the probability $p(E)\Delta E$ that the system has energy between E and $E + \Delta E$? \square

In addition to the relation of the mean energy to $\partial \ln Z / \partial \beta$, we can express the mean pressure \bar{P} in terms of $\partial \ln Z / \partial V$. If the system is in microstate s , then a quasistatic change dV in the volume produces the energy change

$$dE_s = \left(\frac{dE_s}{dV} \right)_{T,N} dV = -\pi_s dV. \quad (4.90)$$

The quantity dE_s in (4.90) is the work done on the system in microstate s to produce the volume change dV . The relation (4.90) defines the contribution to the pressure $\pi_s = -dE_s/dV$ of the system in microstate s .⁸ Hence, the mean pressure of the system is given by

$$\bar{P} = - \sum_s \frac{dE_s}{dV} P_s = \sum_s \pi_s P_s. \quad (4.91)$$

From (4.79), (4.80), and (4.91) we can express the mean pressure as

$$\bar{P} = kT \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}. \quad (4.92)$$

Note that to define the mean pressure we assumed that a small change in the volume does not change the probability distribution P_s of the microstates, but changes only the energy E_s of the microstates. A perturbation of the system will usually induce transitions between the different microstates of the system and hence change the probabilities P_s as well as the energy of the microstates. That is, if the system is initially in microstate s , it will usually not stay in this microstate as the volume is changed. However, if the change occurs sufficiently slowly so that the system can adjust to the change, then the system will remain in microstate s . As discussed in Chapter 2, page 31, such a change is quasistatic.

We can use the relation $\bar{E} = \sum_s P_s E_s$ to write the total change in the energy as

$$d\bar{E} = \sum_s E_s dP_s + \sum_s P_s dE_s. \quad (4.93)$$

The second term in (4.93) can be written as

$$\sum_s P_s dE_s = \sum_s P_s \frac{dE_s}{dV} dV = -\bar{P} dV. \quad (4.94)$$

⁸We have written the pressure in microstate s as π_s rather than P_s or p_s to avoid confusion with the probability.

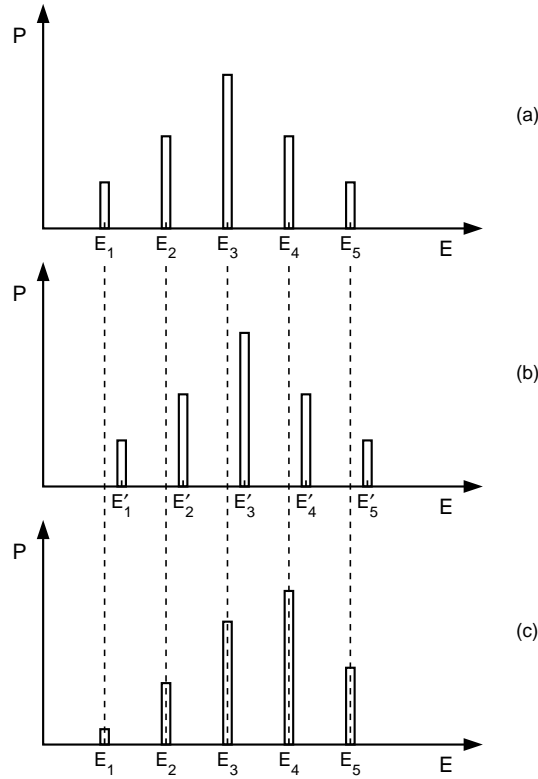


Figure 4.8: (a) Schematic drawing of the eigenstates of a system and their probabilities. (b) The change in the eigenstates of the system when the volume is decreased quasistatically and work is done on the system. No energy is transferred by heating. Note that the probabilities have not changed, and thus the entropy of the system is unchanged. (c) The change in the probabilities of the eigenstates when energy is transferred to the system by heating, and no work is done on the system. In this case the eigenstates are unchanged, but the entropy has increased.

The right-hand side of (4.93) is thus the work done on the system, and we can rewrite (4.93) as

$$d\bar{E} = \sum_s E_s dP_s - \bar{P} dV. \quad (4.95)$$

If we use the fundamental thermodynamic relation (2.128), $dE = TdS - PdV$ (for fixed N), we can identify the first term in (4.95) with the change in entropy of the system. Hence, we have

$$TdS = \sum_s E_s dP_s. \quad (4.96)$$

From (4.96) we see that a change in entropy of the system is related to a change in the probability distribution (see Figure 4.8).

We can use (4.96) to obtain an important expression for the entropy. We rewrite $P_s = e^{-\beta E_s}/Z$

as $E_s = -kT(\ln Z + \ln P_s)$, and substitute this relation for E_s into (4.96):

$$TdS = \sum_s E_s dP_s = -kT \sum_s \ln Z dP_s - kT \sum_s \ln P_s dP_s. \quad (4.97)$$

The first term in (4.97) is zero because the total change in the probability must sum to zero. From (4.97) we write

$$dS = -k \sum_s \ln P_s dP_s, \quad (4.98a)$$

$$= -k \sum_s d(P_s \ln P_s), \quad (4.98b)$$

where we have again used the fact that $\sum dP_s = 0$. We integrate both sides of (4.98b) to obtain the desired result:

$$\boxed{S = -k \sum_s P_s \ln P_s}. \quad (4.99)$$

We have assumed that the constant of integration is zero (see the discussion after (4.100)). The quantity defined by (4.11) and (4.99) is known as the *statistical entropy* in contrast to the *thermodynamic entropy* introduced in Chapter 2. Note the similarity of (4.99) to the uncertainty function defined in (3.36).

The relation (4.99) for S is also applicable to the microcanonical ensemble. If there are Ω accessible microstates, then $P_s = 1/\Omega$ for each microstate because each microstate is equally likely. Hence,

$$S = -k \sum_{s=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega. \quad (4.100)$$

The constant of integration in going from (4.98b) to (4.99) must be set to zero so that S reduces to its form in the microcanonical ensemble. We see that we can interpret (4.99) as the generalization of its microcanonical form with the appropriate weight for each microstate.

The relation (4.99) is of fundamental importance and shows that the entropy is uniquely determined by the probability distribution P_s of the different microstates. Note that complete predictability (only one accessible microstate) implies the vanishing of the entropy. Also as the number of accessible microstates increases, the greater the value of S and hence the higher the degree of unpredictability of the system.

The idea of entropy has come a long way. It was first introduced into thermodynamics as a state function to account for the irreversible behavior of macroscopic systems under certain conditions. The discovery of the connection between this quantity and the probability distribution of the system's microstates was one of the great achievements of Ludwig Boltzmann. It is remarkable that the statistical entropy defined by (4.11) and (4.99) is equivalent to the thermodynamic definition which can be expressed as

$$dS = \frac{dQ}{T}, \quad (4.101)$$

for a quasistatic process. Since then, our understanding of entropy has been extended by Shannon and Jaynes and others to establish a link between thermodynamics and information theory (see

Section 3.4.1). In this context we can say that S is a measure of the lack of information, because the greater the number of microstates that are available to a system in a given macrostate, the less we know about which microstate the system is in.

Although the relation (4.99) is of fundamental importance, we will not use it to calculate the entropy in any of the applications that we consider because it is difficult to calculate the sum. The calculation of the entropy will be discussed in Section 4.7.

The statistical basis of the third law of thermodynamics. We can now see how the third law of thermodynamics (see Section 2.20, page 74) follows from the statistical definition of the entropy. At $T = 0$ the system is in the ground state which we will label by 0. From (4.99) we see that if $P_s = 1$ for microstate 0 and is zero for all other microstates, then $S = 0$. We conclude that $S \rightarrow 0$ as $T \rightarrow 0$ if the system has an unique ground state. This behavior is what is expected for simple systems.

If there are $g(0)$ microstates with the same ground state energy, then the corresponding (residual) entropy is $S(T = 0) = k \ln g(0)$. In this case the ground state is degenerate.⁹ For example, because an electron has spin 1/2, it has two quantum states for each value of its momentum. In practice, there is always a very small, but nonzero magnetic field due to the Earth's magnetic field. Hence, if we could measure the entropy of the ground state of a system of electrons directly, we would find that $S(T = 0) = 0$. However, there are some complex systems for which $g(0) \propto e^N$.¹⁰ We will state the third law of thermodynamics as

The entropy of a system at $T = 0$ is a well-defined constant. For any process that brings a system at $T = 0$ from one equilibrium macrostate to another, the change of entropy $\Delta S = 0$.

Because the entropy can be expressed as $S = \int_0^T (C(T)/T) dT$, we conclude that the heat capacity must go to zero as $T \rightarrow 0$.

Problem 4.27. Entropy of the ground state of a system of electrons

Explain why the entropy associated with the ground state of a system of N electrons would be $kN \ln 2$ in zero magnetic field. \square

4.7 Connection Between Thermodynamics and Statistical Mechanics in the Canonical Ensemble

Just as $S = k \ln \Omega$ gives the fundamental relation between statistical mechanics and thermodynamics for given values of E , V , and N (see Table 4.9), we now determine the connection in the canonical ensemble where T is fixed rather than E . We have seen that the statistical quantity that enters into the calculation of the mean energy and the mean pressure is not Z , but $\ln Z$ (see (4.84) and (4.92)). We also learned in Section 2.21 that the Helmholtz free energy $F = E - TS$ is the

⁹An energy level is said to be degenerate if there are two or more microstates with the same energy.

¹⁰A simple example of a system with a nontrivial number of ground states is the Ising antiferromagnet on the hexagonal lattice. We will discuss this system in Problem 5.14(d). This system has a nonzero entropy at zero temperature.

thermodynamic potential for the variables T , V , and N . Because this set of variables corresponds to the variables specified by the canonical ensemble, it is natural to look for a connection between $\ln Z$ and F , and we will define the latter as

$$\boxed{F = -kT \ln Z}. \quad (\text{statistical mechanics definition of the free energy}) \quad (4.102)$$

We now show that F as defined by (4.102) is equivalent to the thermodynamic definition $F = E - TS$. This equivalence and the relation (4.102) gives the fundamental relation between statistical mechanics and thermodynamics for given values of T , V , and N .

We write the total change in the quantity $\beta F = -\ln Z$ as

$$d(\beta F) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} d\beta - \frac{1}{Z} \frac{\partial Z}{\partial V} dV \quad (4.103a)$$

$$= \bar{E} d\beta - \beta \bar{P} dV, \quad (4.103b)$$

where we have used (4.84) and (4.91) and the fact that F and Z depend on $T(\beta)$ and V . For simplicity, we will ignore the dependence of F and Z on N in this chapter unless otherwise stated. We add and subtract $\beta d\bar{E}$ on the right-hand side of (4.103b) to find

$$d(\beta F) = \bar{E} d\beta + \beta d\bar{E} - \beta d\bar{E} - \beta \bar{P} dV \quad (4.104a)$$

$$= d(\beta \bar{E}) - \beta(d\bar{E} + \bar{P} dV). \quad (4.104b)$$

Hence, we can write

$$d(\beta F - \beta \bar{E}) = -\beta(d\bar{E} + \bar{P} dV). \quad (4.105)$$

From the thermodynamic relation $dE = TdS - \bar{P}dV$ (for fixed N), we can rewrite (4.105) as

$$d(\beta F - \beta \bar{E}) = -\beta(d\bar{E} + \bar{P} dV) = -\beta T dS = -dS/k. \quad (4.106)$$

If we integrate (4.106), we find

$$S/k = \beta(\bar{E} - F) + \text{constant}, \quad (4.107)$$

or

$$F = \bar{E} - TS + \text{constant}. \quad (4.108)$$

If we make the additional assumption that the free energy should equal the internal energy of the system at $T = 0$, we can set the constant in (4.108) equal to zero, and we obtain

$$F = \bar{E} - TS. \quad (4.109)$$

Equation (4.109) is equivalent to the thermodynamic definition of the Helmholtz free energy with E replaced by \bar{E} . In the following, we will often write E instead of \bar{E} because the distinction will be clear from the context.

In Section 2.21 we showed that the Helmholtz free energy F is the natural thermodynamic potential for given values of T , V , and N and that

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}. \quad (4.110)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad (4.111)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}. \quad (4.112)$$

These relations still hold with $F = -kT \ln Z$.

We have found that if we start with the statistical mechanical relation $F = -kT \ln Z$ (see (4.102)), we obtain the thermodynamic relation $F = E - TS$ (see (4.109)). It is instructive to start with the latter and show that it implies that $F = -kT \ln Z$. We substitute $E = -\partial \ln Z / \partial \beta$ and the relation $S = k\beta^2(\partial F / \partial \beta)$ (see (4.110)) and find

$$F = E - TS = -\frac{\partial \ln Z}{\partial \beta} - \beta \left(\frac{\partial F}{\partial \beta} \right)_{V,N}. \quad (4.113)$$

We rewrite (4.113) as

$$F + \beta \left(\frac{\partial F}{\partial \beta} \right)_{V,N} = \left(\frac{\partial \beta F}{\partial \beta} \right)_{V,N} = -\frac{\partial \ln Z}{\partial \beta}. \quad (4.114)$$

If we integrate both sides of (4.114), we find (up to a constant) that

$$F = -kT \ln Z. \quad (4.115)$$

4.8 Simple Applications of the Canonical Ensemble

To gain experience with the canonical ensemble, we first consider some simple examples for which we can do the needed sums over microstates explicitly. In all of these examples, the goal is to calculate the partition function. The usual procedure is to then calculate the free energy using (4.102), the entropy using (4.110), and the mean energy using (4.84). (In these simple examples, the volume of the system will not be relevant, so we will not calculate the pressure.) In principle, we can follow this “recipe” for any physical system, but we will find starting in Chapter 5 that summing over the microstates to evaluate the partition function is usually a formidable task and can be done exactly in only a few cases.

Example 4.2. Two distinguishable particles

Consider a system consisting of two distinguishable particles. Each particle can be in one of two microstates with single particle energies 0 and Δ . The quantity Δ is called the energy gap. The system is in equilibrium with a heat bath at temperature T . What are the thermodynamic properties of the system?

Solution. The microstates of this two-particle system are $(0, 0)$, $(0, \Delta)$, $(\Delta, 0)$, and (Δ, Δ) . The partition function Z_2 is given by

$$Z_2 = \sum_{s=1}^4 e^{-\beta E_s} \quad (4.116a)$$

$$= 1 + 2e^{-\beta\Delta} + e^{-2\beta\Delta} \quad (4.116b)$$

$$= (1 + e^{-\beta\Delta})^2. \quad (4.116c)$$

We can express Z_2 in terms of Z_1 , the partition function for one particle:

$$Z_1 = \sum_{s=1}^2 e^{-\beta \epsilon_s} = 1 + e^{-\beta\Delta}. \quad (4.117)$$

By comparing the forms of (4.116c) and (4.117), we find that

$$Z_2 = Z_1^2. \quad (4.118)$$

What do you expect the relation is between Z_N , the partition function for N noninteracting distinguishable particles, and Z_1 ?

Note that if the two particles were indistinguishable, there would be three microstates if the particles were bosons and one microstate if the particles were fermions, and the relation (4.118) would not hold.

Because Z_2 is simply related to Z_1 , we can consider the statistical properties of a system consisting of one particle with Z_1 given by (4.117). From (4.79) we find the probability that the system is in each of its two possible microstates is given by:

$$P_1 = \frac{1}{Z_1} = \frac{1}{1 + e^{-\beta\Delta}} \quad (4.119a)$$

$$P_2 = \frac{e^{-\beta\Delta}}{Z_1} = \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \quad (4.119b)$$

The average energy is given by

$$\bar{e} = \sum_{s=1}^2 P_s \epsilon_s = \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \quad (4.120)$$

We will use a lower case symbol to denote the results for one particle.

Of course, \bar{e} could also be found from the relation $\bar{e} = -\partial \ln Z_1 / \partial \beta$. For our example we have

$$Z_1 = 1 + e^{-\beta\Delta} \quad (4.121)$$

and

$$\frac{\partial Z_1}{\partial \beta} = -\Delta e^{-\beta\Delta}. \quad (4.122)$$

Hence

$$\bar{e} = -\frac{\partial}{\partial \beta} \ln Z_1 = -\frac{1}{Z_1} \frac{\partial Z_1}{\partial \beta} = \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}, \quad (4.123)$$

in agreement with (4.120). The energy of N noninteracting, distinguishable particles of the same type is given by $\bar{E} = N\bar{e}$.

It is easy to calculate f , the free energy per particle, from the partition function in (4.116c). We have

$$f = -kT \ln Z_1 = -kT \ln[1 + e^{-\beta\Delta}]. \quad (4.124)$$

Because we have already calculated f and \bar{e} , we can calculate s , the entropy per particle, from the relation $f = e - Ts$, or $s = (e - f)/T$. Alternatively, we can calculate s by taking the temperature

derivative of the free energy (see (4.110)):

$$s = -\left(\frac{\partial f}{\partial T}\right)_V = k \ln[1 + e^{-\beta\Delta}] + kT \frac{d\beta}{dT} \frac{\partial}{\partial \beta} \ln[1 + e^{-\beta\Delta}] \quad (4.125a)$$

$$= k \ln[1 + e^{-\beta\Delta}] + kT \left(\frac{-1}{kT^2}\right) \frac{-\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \quad (4.125b)$$

$$= k \ln[1 + e^{-\beta\Delta}] + \left(\frac{\Delta}{T}\right) \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \quad (4.125c)$$

$$= k \ln[1 + e^{-\beta\Delta}] + k \frac{\beta\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \quad (4.125d)$$

The behavior of the various thermodynamic properties of this system are explored in Problem 4.47. \diamond

Example 4.3. The thermodynamic properties of a single one-dimensional harmonic oscillator in equilibrium with a heat bath at temperature T

Solution. The energy levels of a single harmonic oscillator in one dimension are given by

$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega. \quad (n = 0, 1, 2, \dots) \quad (4.126)$$

The corresponding partition function is

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \quad (4.127a)$$

$$= e^{-\beta\hbar\omega/2} (1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots) = e^{-\beta\hbar\omega/2} (1 + x + x^2 + \dots), \quad (4.127b)$$

where $x = e^{-\beta\hbar\omega}$. The infinite sum in (4.127b) is a geometric series in x and can be summed using the result that $1 + x + x^2 + \dots = 1/(1 - x)$ (see Appendix A). The result is

$$Z_1 = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}, \quad (4.128)$$

and

$$\ln Z_1 = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega}). \quad (4.129)$$

\diamond

Problem 4.28. Thermodynamic properties of a system of harmonic oscillators

(a) Show that for one oscillator

$$f = \frac{1}{2}\hbar\omega + kT \ln(1 - e^{-\beta\hbar\omega}) \quad (4.130)$$

$$s = k \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega}) \right] \quad (4.131)$$

$$\bar{e} = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right]. \quad (4.132)$$

Equation (4.132) is Planck's formula for the mean energy of an oscillator at temperature T . The heat capacity is discussed in Problem 4.50.

- (b) Given the result (4.132) what is the mean energy of a system of N harmonic oscillators in equilibrium with a heat bath at temperature T ?
- (c) Compare your answer with the result for the energy of N harmonic oscillators calculated in the microcanonical ensemble in Problem 4.22. Do the two ensembles give identical results? \square

Equation (4.80) for Z is a sum over all the microstates of the system. Because the energies of different microstates may be the same, we can group together microstates with the same energy and write (4.80) as

$$Z = \sum_{\text{levels } \ell} \Omega(E_\ell) e^{-\beta E_\ell}, \quad (4.133)$$

where $\Omega(E_\ell)$ is the number of microstates with energy E_ℓ . The sum in (4.133) is over all the energy levels of the system, rather than over all the microstates of the system.

Example 4.4. Consider a three level single particle system with six microstates with energies 0, ϵ , ϵ , ϵ , 2ϵ , and 2ϵ . What is $\Omega(\epsilon)$ for this system? What is the mean energy of the system if it is in equilibrium with a heat bath at temperature T ?

Solution. In this case we have $\Omega(0) = 1$, $\Omega(\epsilon) = 3$, and $\Omega(2\epsilon) = 2$. The partition function is given by (see (4.133))

$$Z_1 = 1 + 3e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}. \quad (4.134)$$

Hence, the mean energy of a single particle is given by

$$\bar{e} = \epsilon \frac{3e^{-\beta\epsilon} + 4e^{-2\beta\epsilon}}{1 + 3e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}. \quad (4.135)$$

What is the energy of N such particles? \diamond

4.9 An Ideal Thermometer

The temperature of a system is an abstract quantity in part because we don't have a direct way to measure it. Instead, we need to measure some other quantity such as the pressure in a container or the expansion of a metal, and then calibrate these measurements with the temperature by assuming that the measurements change in some known way with temperature. We now discuss a simple thermometer which gives a direct measure of the temperature. This thermometer has only one property, its energy, and can be realized in a computer simulation.

As discussed in Section 2.4 (page 34), an ideal thermometer interacts very weakly with the system of interest, but strongly enough to obtain an accurate measurement. Also, there needs to be a known relation between some property of the thermometer and the temperature.

Consider a system of one particle which we will call a *demon* that can exchange energy with another system (see page 17).¹¹ Here the demon will play the role of a thermometer, and the other

¹¹ "Demons" have a rich history in statistical mechanics. See for example, Harvey Leff and Andrew F. Rex, editors, *Maxwell's Demon 2: Entropy, Classical and Quantum Information, Computing*, CRC Press (2003).

system, which we will call “the system,” is much larger and plays the role of a heat bath. We will use the demon to measure the temperature of the heat bath. As long as almost all of the energy resides in the heat bath, the temperature of the heat bath will not change. The demon obeys the following rules or algorithm:

1. Set up an initial microstate of the system with the desired total energy E and assign an initial energy E_d to the demon. (For convenience the initial demon energy is usually set to zero.)
2. Make a trial change in the microstate. For example, for the Einstein solid, choose a particle at random and randomly increase or decrease its energy by one. For the Ising model, flip a spin chosen at random.
3. Compute the change in energy of the system, ΔE . If $\Delta E \leq 0$, accept the change, and increase the energy of the demon by $|\Delta E|$. If $\Delta E > 0$, accept the change if the demon has enough energy to give to the system, and reduce the demon’s energy by ΔE . The only constraint is that the demon’s energy must remain greater than a lower bound which we take to be zero. If a trial change is not accepted, the existing microstate is counted in the averages. In either case the total energy E of the system plus the energy E_d of the demon remains constant.
4. Repeat steps 2 and 3 many times.
5. Compute the averages of the quantities of interest once the system and the demon have reached equilibrium.

The demon can trade energy with the system as long as its energy remains greater than its lower bound, which we have chosen to be zero. The demon is a facilitator that allows the particles (or spins) in the system to indirectly trade energy with one another.

In Problems 4.29 and 4.31 we use the demon algorithm to determine the mean energy of the demon and the probability that it is in a particular microstate.

Problem 4.29. The demon and the ideal classical gas

Consider a demon that exchanges energy with an ideal classical gas of N identical particles of mass m in three dimensions. Because the energy of a particle in an ideal gas depends only on its speed, the positions of the particles are irrelevant in this case. The demon chooses a particle at random and changes its velocity in a particular direction by an amount, δ , chosen at random between $-\delta_m$ and δ_m . The change in energy of the system is $\Delta E = \frac{1}{2}[(v + \delta)^2 - v^2]$; we have chosen units so that $m = 1$. The parameter δ_m is arbitrary. The program `TemperatureMeasurementIdealGas` implements the demon algorithm for an ideal classical gas in d dimensions. For simplicity, the program initially assigns each particle in the gas the same initial velocity \mathbf{v} in the x -direction; $|\mathbf{v}|$ is chosen so that the initial energy of the system is E . The initial demon energy is set equal to zero.

- (a) Before you do the simulation, sketch the energy-dependence of the probability $p(E_d)\Delta E_d$ that the demon has an energy between E_d and $E_d + \Delta E_d$. Is $p(E_d)$ an increasing or decreasing function of E_d or does it have a maximum at some value of E_d ?

- (b) Choose $d = 3$ and $N = 40$ and $E = 40$ so that $E/N = 1$. Determine $\overline{E_d}$, the mean energy of the demon, and \overline{E}/N , the mean energy per particle of the system after the demon and the system have reached equilibrium. (Use the **Zero** button.) Then choose other combinations of N and E and determine the relation between $\overline{E_d}$ and \overline{E}/N .
- (c) We know that the mean energy of an ideal classical gas in three dimensions is equal to $3NkT/2$ (see (4.65)), where T is the temperature of the system. Use this relation and the values of \overline{E}/N that you found in part (b) to estimate the temperature of the gas. What is the relation of the temperature that you found in this way to $\overline{E_d}$? (Use units such that $k = 1$.)
- (d) Run for a sufficient number of trials so that the form of $p(E_d)$ is well defined, and verify the exponential form of $p(E_d)$.¹² Compare your results for the temperature that you found in part (c) with value of $1/\beta$ that you determined from the exponential fit of $p(E_d)$. Then assume that $\beta = 1/kT$ and compare the values of the temperature that you obtained.
- (e) We will show in Problem 4.30 that $\overline{E_d} = kT$ given the exponential form of the probability density $p(E_d)$ that you found in part (d) and the fact that E_d is a continuous variable. How well do your simulation results for $\overline{E_d}$ agree with this prediction?
- (f) How do your results change for an ideal gas in two and three dimensions?
- (g) Explain why the form of $p(E_d)$ is given by the Boltzmann distribution. What property (properties) of the demon make it an ideal thermometer?
- (h) Compare the initial mean velocity of the particles in the system to the mean value after equilibrium has been established. What is form of the distribution of the velocities in equilibrium? \square

Problem 4.30. The temperature dependence of the mean demon energy: Continuous case

A demon exchanges energy with an ideal classical gas of N particles in three dimensions (see Problem 4.29). What is the mean energy of the demon?

In this case the demon energy is a continuous variable. Hence, we can analytically determine the relation between the mean demon energy and the temperature:

$$\overline{E_d} = \frac{\int_0^\infty E_d e^{-\beta E_d} dE_d}{\int_0^\infty e^{-\beta E_d} dE_d}. \quad (4.136)$$

- (a) Explain why the relation (4.136) for the demon energy is reasonable and determine the temperature dependence of $\overline{E_d}$.
- (b) Would this temperature dependence be different if the gas is in one or two dimensions? Would the temperature dependence change if the particles in the gas interacted with one another? \square

Problem 4.31. The demon and the Einstein solid

Consider a demon that exchanges energy with an Einstein solid of N particles. The demon selects a particle at random and randomly changes its energy by ± 1 consistent with the constraint that

¹²Choose **Data Tool** under the **Views** menu and click **OK**. Select the **Fit Box** and then select **Fit Builder**. Add two fit parameters, say a and b , and then add the expression $a*\exp(-b*x)$.

$E_d \geq 0$. In this case the energy of each particle in the system also must remain nonnegative. Why? If a trial change is not accepted, the existing microstate is counted in all averages. Use the program `TemperatureMeasurementEinsteinSolid` to do the simulations.

- Choose $N = 40$ and $E = 200$. What is the mean energy of the demon after equilibrium between the demon and the system has been established? Compare the values of $\overline{E_d}$ and \overline{E}/N . Fix $N = 40$ and change E . How does $\overline{E_d}$ depend on \overline{E}/N ?
- Compute the probability $P(E_d)$ for various values of E and N . Fit your results to the form $\ln P(E_d) = -\beta E_d + \text{constant}$, where β is a parameter. Is β simply related to the mean demon energy?
- Explain why the form of $P(E_d)$ is given by the Boltzmann distribution. What property of the demon appears to be universal? \square

Problem 4.32. The temperature dependence of the mean demon energy for an Einstein solid. A demon exchanges energy with an Einstein solid of N particles (see Problem 4.31).

- Explain why the energy of the demon is restricted to integer values.
- Explain why the demon's mean energy is given by

$$\overline{E_d} = \frac{\sum_{n=0}^{\infty} n e^{-\beta n}}{\sum_{n=0}^{\infty} e^{-\beta n}}. \quad (4.137)$$

- Do the sums in (4.137) to determine the temperature dependence of $\overline{E_d}$. (It is necessary to evaluate only the sum in the denominator of (4.137). The numerator can be determined by an appropriate derivative of the result for the denominator. See Example 4.3.)
- Why is the temperature dependence of $\overline{E_d}$ different for an ideal gas and an Einstein solid?
- *In what limit does the temperature dependence become the same? \square

4.10 Simulation of the Microcanonical Ensemble

How can we implement the microcanonical ensemble on a computer? One way to do so for a classical system of particles is to use the method of molecular dynamics (see Section 1.4) which is based on the numerical solution of Newton's equations of motion. We first choose initial conditions for the positions and velocities of each particle that are consistent with the desired values of E , V , and N . The numerical solution of Newton's equations generates a trajectory in $6N$ -dimensional phase space (for a system in three spatial dimensions). Each point on the trajectory represents a microstate of the microcanonical ensemble with the additional condition that the momentum of the center of mass is fixed. The averages over the phase space trajectory represent a time average.

To do such a simulation we need to be careful to choose a representative initial condition. It could happen that most of the microstates consistent with the desired values of E , V and N are not

easy to reach from a specific microstate, and hence the system might spend a long time in similar non-representative microstates. Because molecular dynamics simulates systems for physical times that are very short (the longest time we can simulate is $\approx 10^{-6}$ s), the system might not reach equilibrium within a reasonable amount of computer time if we do not choose the initial microstate properly.

Our assumption that a molecular dynamics simulation generates microstates consistent with the microcanonical ensemble is valid as long as a representative sample of the accessible microstates can be reached during the duration of the simulation. Such a system is said to be *ergodic*.

As we will justify further in Section 6.2.1, we can identify the temperature of a system of interacting classical particles with the kinetic energy per particle using the relation (4.65). (For the ideal gas the total energy is the kinetic energy.) If we were to do a molecular dynamics simulation, we would find that the total energy is approximately constant (it would be a constant if we could numerically solve the equations of motion exactly), and the kinetic energy and hence the temperature fluctuates as is expected for the microcanonical ensemble. The mean temperature of the system becomes well defined if the system is in equilibrium, the number of particles in the system is sufficiently large, and the simulation is done for a sufficiently long time.

What if we wish to simulate a system at fixed total energy for which Newton's equations of motion is not applicable? For example, there is no dynamics for the Einstein solid in which the particles have only integer values of the energy. Another general way of generating representative microstates is to use a *Monte Carlo* method. As an example, the relevant variables for the Einstein solid are the quantum numbers of each particle such that their sum equals the desired total energy E . Given a set of quantum numbers, how do we generate another set of unbiased quantum numbers with the same energy? Because we want to generate a representative sample of the accessible microstates, we need to make all changes at random. One possibility is to choose two particles at random and make trial changes in their energy by ± 1 such that the total energy is unchanged.

A more interesting example is the Ising model in which the spins interact with their nearest neighbors with an energy $+J$ if the spins are parallel and energy $-J$ if the spins are antiparallel (see Section 1.9.3). We will discuss the Ising model in more detail in Chapter 5. Here it is sufficient to understand that the individual spins interact with one another.

The condition that the total energy be fixed makes sampling the accessible microstates of the Ising model difficult. If we choose a spin at random and flip it, the change will frequently change the energy of the system. We can circumvent this difficulty by relaxing the condition that the total energy be fixed by adding to the system of N particles an extra degree of freedom called the demon, as we discussed in Section 4.9. The total energy of the demon plus the original system is fixed. Because the demon is one particle out of $N + 1$, the fluctuations in the energy of the original system are order $1/N$, which goes to zero as $N \rightarrow \infty$. Hence, the demon simulation can be viewed either as a means of illustrating an ideal thermometer by focusing on the demon as a system in the canonical ensemble or as a way of simulating the microcanonical ensemble by focusing on the particles in the system interacting with the demon.

4.11 Simulation of the Canonical Ensemble

Suppose that we wish to simulate a system that is in equilibrium with a heat bath at temperature T . One way to do so is to start with an arbitrary microstate of energy E_s and weight it by its relative probability $e^{-\beta E_s}$. For example, we could generate another microstate of an Einstein solid by choosing a particle at random and changing its energy by ± 1 at random. If we repeated this process M times, the mean energy of the system could be estimated by

$$\bar{E}(T) = \frac{\sum_{s=1}^M E_s e^{-\beta E_s}}{\sum_{s=1}^M e^{-\beta E_s}}, \quad (4.138)$$

where E_s is the energy of microstate s and the sum is over the M microstates that have been generated at random. However, this procedure would be very inefficient because the M states would include many high energy states whose weight in averages such as (4.138) would be exponentially small.

One way to make the sampling procedure more efficient is to generate microstates with probabilities proportional to their weight, that is, proportional to $e^{-\beta E_s}$. In this way we would generate microstates with the highest probability. Such a sampling procedure is known as *importance sampling*. The simplest and most common method of importance sampling in statistical mechanics is known as the *Metropolis algorithm*. This algorithm is based on the fact that the ratio of the probability that the system is in microstate j with energy E_j to the probability of being in microstate i with energy E_i is $p_j/p_i = e^{-\beta(E_j - E_i)} = e^{-\beta \Delta E}$, where $\Delta E = E_j - E_i$. We may interpret this ratio as the probability of a transition from microstate i to microstate j . If $\Delta E < 0$, the ratio $e^{-\beta \Delta E}$ is greater than one, and the probability is set to one. The Metropolis algorithm can be summarized as follows:¹³

1. Choose an initial microstate, for example, random initial energies for each particle in an Einstein solid or random positions in a system of particles interacting via the Lennard-Jones potential. Also fix the desired temperature T of the system.
2. Make a trial change in the microstate. For the Einstein solid, choose a particle at random and randomly change its energy by ± 1 . For a system of interacting particles, change the position of a particle by a small random amount. Compute the change in energy of the system, ΔE , corresponding to this change. If $\Delta E < 0$, then accept the change. If $\Delta E > 0$, accept the change with probability $w = e^{-\beta \Delta E}$. To do so, generate a random number r uniformly distributed in the unit interval. If $r \leq w$, accept the new microstate; otherwise, retain the previous microstate.
3. Repeat step 2 many times.
4. Compute the averages of the quantities of interest after the system has reached equilibrium.

Problem 4.33. Simulation of the Einstein solid in equilibrium with a heat bath

Use the Metropolis algorithm to simulate an Einstein solid of N particles at a temperature T . The program at `TemperatureMeasurementEinsteinSolid` implements the Metropolis algorithm

¹³The Metropolis algorithm is justified in the paper by Tobochnik and Gould (see the references at the end of this chapter).

by choosing a particle at random and randomly increasing or decreasing its energy by one unit. If the energy is decreased, the change is accepted. If the energy is increased, the program generates a number r at random in the unit interval and accepts the change if $r \leq e^{-\beta}$, where $\beta = 1/T$. (As usual, we choose units such that Boltzmann's constant $k = 1$.) If a trial change is not accepted, the existing microstate is counted in all averages. These process is repeated many times until the various averages become well defined.

- (a) Choose $N = 20$ and $\beta = 1$. Does the energy of the system eventually reach a well defined average? If so, vary β and determine $\bar{E}(T)$.
- (b) Compare your results to the analytical results found in Example 4.3. \square

We will consider many other applications of the Metropolis algorithm in later chapters.

4.12 Grand Canonical Ensemble (Fixed T , V , and μ)

In Section 4.6 we derived the Boltzmann probability distribution for a system in equilibrium with a heat bath at temperature T . We now generalize the heat bath to a reservoir that can exchange particles as well as energy and find the probability distribution for a system in equilibrium with the reservoir at temperature T and chemical potential μ . In this case the role of the reservoir is to fix the chemical potential as well as the temperature. Hence the mean number of particles as well as the mean energy are determined. This ensemble is known as the *grand canonical ensemble*.

As before, the composite system is isolated with total energy E , total volume V , and total number of particles N . The probability that the (sub)system is in microstate s with energy E_s and N_s particles is given by (see (4.75))

$$P_s = \frac{1 \times \Omega_b(E - E_s, N - N_s)}{\sum_s \Omega_b(E - E_s, N - N_s)}. \quad (4.139)$$

The difference between (4.75) and (4.139) is that we have allowed both the energy and the number of particles of the system of interest to vary. As before, we take the logarithm of both sides of (4.139) and exploit the fact that $E_s \ll E$ and $N_s \ll N$. We have

$$\ln P_s \approx \text{constant} - E_s \left(\frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \right)_{E_b=E} - N_s \left(\frac{\partial \ln \Omega_b(N_b)}{\partial N_b} \right)_{N_b=N}, \quad (4.140)$$

where $E_b = E - E_s$ and $N_b = N - N_s$. If we substitute $\beta = \partial \ln \Omega_b / \partial E$ (see (4.78)) and $\beta\mu = -\partial \ln \Omega_b / \partial N$ (see (2.120)), we obtain

$$\ln P_s = \text{constant} - \frac{E_s}{kT} + \frac{\mu N_s}{kT}, \quad (4.141)$$

or

$$\boxed{P_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}}. \quad (\text{Gibbs distribution}) \quad (4.142)$$

Equation (4.142) is the Gibbs probability distribution for a variable number of particles. This distribution gives the probability that the system is in microstate s with energy E_s and N_s particles. The *grand partition function* Z_G in (4.142) is found from the normalization condition

$$\sum_s P_s = 1. \quad (4.143)$$

Hence, we obtain

$$\boxed{Z_G = \sum_s e^{-\beta(E_s - \mu N_s)}}. \quad (\text{grand partition function}) \quad (4.144)$$

In analogy to the relations we found in the canonical ensemble, we expect that there is a simple relation between the Landau potential defined in (2.163) and the grand partition function. Because the derivation of this relation proceeds as in Sec. 4.6, we simply give the relation:

$$\boxed{\Omega = -kT \ln Z_G}. \quad (4.145)$$

Example 4.5. Absorption of atoms on surface sites

Consider a surface with sites that can absorb atoms. Each site can be empty or have at most one absorbed atom. The energy of the site is zero if no atom is present and ϵ if one atom is present. The occupancy of the sites is not correlated. What is the mean number of atoms that are absorbed assuming that the surface is in equilibrium with a reservoir at temperature T and chemical potential μ ?

Solution. Because the sites are not correlated, we consider a system of one site. The system has two states with energy 0 and ϵ , and its grand partition function is given by

$$Z_G = 1 + e^{-\beta(\epsilon - \mu)}. \quad (4.146)$$

The probability that one atom is absorbed is

$$p = \frac{e^{-\beta(\epsilon - \mu)}}{Z_G} = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}. \quad (4.147)$$

The mean number of atoms absorbed is

$$\bar{n} = 0 \times (1 - p) + 1 \times p = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}. \quad (4.148)$$

Suppose that we know that $\bar{n} = 0.6$ at $T = 3$ (in units such that $k = 1$). What is the chemical potential μ in this case? Choose $\epsilon = 1$ for simplicity.

We solve for μ from (4.148) and find that

$$\mu = \epsilon - kT \ln(\bar{n}^{-1} - 1) = 1 - 3 \ln \frac{2}{3} = 1 + 3 \ln \frac{3}{2} \approx 2.22. \quad (4.149)$$

◇

4.13 *Entropy is not a Measure of Disorder

Many texts and articles for the scientifically literate refer to entropy as a measure of “disorder” or “randomness.” This interpretation is justified by the relation, $S = k \ln \Omega$. The argument is that an increase in the disorder in a system corresponds to an increase in Ω . Sometimes a reference is made to a situation such as the tendency of students’ rooms to become messy. There are two problems with this interpretation – it adds nothing to our understanding of entropy and it is inconsistent with our naive understanding of structural disorder.

We have already discussed the interpretation of the entropy as a measure of the uncertainty or lack of information. Thus, we already have a precise definition of entropy and can describe a student’s messy room as having a high entropy because of our lack of information about the location of a particular paper or article of clothing. We could define disorder as lack of information, but such a definition does not help us to understand entropy any better because it does not provide an independent understanding of disorder.

The other problem with introducing the term disorder to describe entropy is that it can lead to incorrect conclusions. In the following we will describe two examples where the crystalline phase of a given material has a higher entropy than the liquid phase. Yet you would probably agree that a crystal is more ordered than a liquid. So how can a crystal have a higher entropy? The following analogy might be helpful.

Suppose that you are going on a short trip and you need to pack your suitcase with only a few articles.¹⁴ In this case the volume of the suitcase is much greater than the total volume of the articles you wish to pack, and you would probably just randomly throw the articles into the suitcase. Placing the articles in an ordered arrangement would require extra time and the ordered arrangement would probably be lost during your trip. In statistical mechanics terms we say that there are many more ways in which the suitcase can be packed in a disordered arrangement than the ordered one. Hence, we could conclude that the disordered macrostate has a higher entropy than the ordered macrostate. This low density case is consistent with the naive association of entropy and disorder.

Now suppose that you are going on a long trip and you need to pack many articles in the same suitcase, that is, the total volume of the articles to be packed is comparable to the volume of the suitcase. In this high density case you know that randomly throwing the articles into the suitcase won’t allow you to shut the suitcase. Such a configuration is incompatible with the volume constraints of the suitcase. If you randomly throw the articles in the suitcase many times, you would find only a few configurations that would allow you to close the suitcase. In contrast, if you pack the articles in a neat and ordered arrangement, the suitcase can be closed. Also there are many such configurations that would satisfy the constraints. We conclude that the number of ordered arrangements of the articles in the suitcase is greater than the number of disordered arrangements. Therefore an ordered arrangement in the high density suitcase has a higher entropy than a structurally disordered state. The association of disorder with entropy is not helpful here.

The suitcase analogy is an example of an *entropy-driven phase transition* from a low to a high density macrostate because energy did not enter into our considerations at all. Another example of system that exhibits an entropy-driven transition is a system of hard disks. In this seemingly

¹⁴This example is due to Laird (see the references).

simple model the interaction between two particles is given by

$$u(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma), \end{cases} \quad (4.150)$$

where σ represents the diameter of the hard disks. For this model, only non-overlapping configurations are allowed and so the potential energy is zero. Hence, the internal energy is solely kinetic and the associated contribution of the energy to the free energy is the ideal gas part which depends only on the temperature and the density. Hence, the difference in the free energy $\Delta F = \Delta E - T\Delta S$ between a hard sphere crystal and a hard sphere fluid at the same density and temperature is equal to $-T\Delta S$.

In the following problem we will do an exploratory simulation of a system of hard disks that suggests that there is a transition from a fluid at low density to a crystal at high density. (We use the term *fluid* when there is no distinction between a gas and a liquid.) That is, at some density ΔF must become negative, which can occur only if $\Delta S = S_{\text{crystal}} - S_{\text{fluid}}$ is positive. We conclude that at high density the entropy of the crystal must be greater than that of a fluid at equal temperature and density for a fluid-solid (freezing) transition to exist.

Problem 4.34. Simulation of hard disks

The dynamics of a system of hard disks are straightforward in principle because the particles move in straight lines in between collisions. The program `HardDisksMD` finds when the next two particles are going to collide and moves the particles accordingly.

- (a) Run the simulation for the default parameters and record the density and the results for PA/NkT and the temperature. Is the temperature a useful quantity for hard disks? Does it fluctuate during the simulation. If not why not? Does the pressure P fluctuate?
- (b) Compute PA/NkT as a function of density for a fixed number of particles. Is there any evidence of a phase transition where the slope of the pressure with respect to density changes abruptly? □

4.14 Supplementary Notes

4.14.1 The volume of a hypersphere

In the following we derive the expression (4.46) for the volume of a hypersphere of n dimensions. As in (4.45) the volume is given formally by

$$V_n(R) = \int_{x_1^2 + x_2^2 + \dots + x_n^2 < R^2} dx_1 dx_2 \dots dx_n. \quad (4.151)$$

Because $V_n(R) \propto R^n$ for $n = 2$ and 3 , we expect that V_n is proportional to R^n . Hence, we write

$$V_n = C_n R^n, \quad (4.152)$$

where C_n is the unknown constant of proportionality that we wish to find. We rewrite the volume element $dV_n = dx_1 dx_2 \cdots dx_n$ as

$$dV_n = dx_1 dx_2 \cdots dx_n = S_n(R) dR = nC_n R^{n-1} dR, \quad (4.153)$$

where $S_n = nC_n R^{n-1}$ is the surface area of the hypersphere. For example, for $n = 3$ we have $dV_3 = 4\pi R^2 dR$ and $S_3 = 4\pi R^2$. To find C_n for general n , consider the identity (see Appendix A)

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n e^{-(x_1^2 + \cdots + x_n^2)} = \left[\int_{-\infty}^{\infty} dx e^{-x^2} \right]^n = \pi^{n/2}. \quad (4.154)$$

The left-hand side of (4.154) can be written as

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n e^{-(x_1^2 + \cdots + x_n^2)} = \int_0^{\infty} dR S_n(R) e^{-R^2} \quad (4.155a)$$

$$= nC_n \int_0^{\infty} dR R^{n-1} e^{-R^2}. \quad (4.155b)$$

We can relate the integral in (4.155b) to the Gamma function $\Gamma(n)$ defined by the relation

$$\Gamma(n) = \int_0^{\infty} dx x^{n-1} e^{-x}. \quad (4.156)$$

The relation (4.156) holds for $n > -1$ and whether or not n is an integer. We make the change of variables $u = R^2$ so that

$$I_n = \frac{1}{2} nC_n \int_0^{\infty} du u^{n/2-1} e^{-u} = \frac{1}{2} nC_n \Gamma(n/2). \quad (4.157)$$

A comparison of (4.157) with (4.154) yields the desired relation

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(\frac{n}{2})} = \frac{\pi^{n/2}}{(n/2)\Gamma(\frac{n}{2})}. \quad (4.158)$$

It follows that

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(\frac{n}{2})} R^n. \quad (4.159)$$

4.14.2 Fluctuations in the canonical ensemble

To gain more insight into the spread of energies that are actually observed in the canonical ensemble, we determine the probability $p(E)\Delta E$ that a system in equilibrium with a heat bath at temperature T has energy E in the range E to $E + \Delta E$. In most macroscopic systems the number of microstates with the same energy is large. In such a case the probability that the system is in any of the microstates with energy E can be written as

$$\frac{\Omega(E)e^{-\beta E}}{\sum_{\text{levels}} \Omega(E)e^{-\beta E}}, \quad (4.160)$$

where $\Omega(E)$ is the number of microstates with energy E . As in (4.133) the sum in the denominator in (4.160) is over the different energy levels of the system. In the thermodynamic limit $N, V \rightarrow \infty$, the spacing between consecutive energy levels becomes very small and we can regard E as a continuous variable. We write $p(E)dE$ for the probability that the system in the range E and $E + dE$ and let $g(E)dE$ be the number of microstates between E and $E + dE$. (The function $g(E)$ is the density of states and is the same function discussed in Section 4.3.) Hence, we can rewrite (4.160) as

$$p(E) dE = \frac{g(E)e^{-\beta E} dE}{\int_0^\infty g(E)e^{-\beta E} dE}. \quad (4.161)$$

As we did on page 138 we can find an approximate form of $p(E)$ by expanding $p(E)$ about $E = \tilde{E}$, the most probable value of E . To do so, we evaluate the derivatives $\partial(\ln p)/\partial E$ and $\partial^2 \ln p/\partial E^2$ using (4.161):

$$\left(\frac{\partial \ln p}{\partial E}\right)_{E=\tilde{E}} = \left(\frac{\partial \ln g}{\partial E}\right)_{E=\tilde{E}} - \beta = 0, \quad (4.162)$$

and

$$\left(\frac{\partial^2 \ln p}{\partial E^2}\right)_{E=\tilde{E}} = \left(\frac{\partial^2 \ln g}{\partial E^2}\right)_{E=\tilde{E}}. \quad (4.163)$$

We have

$$\left(\frac{\partial^2 \ln g}{\partial E^2}\right)_{E=\tilde{E}} = \frac{\partial}{\partial E} \left(\frac{\partial \ln g}{\partial E}\right)_{E=\tilde{E}} = \frac{\partial \beta}{\partial E}. \quad (4.164)$$

Finally, we obtain

$$\frac{\partial \beta}{\partial E} = -\frac{1}{kT^2} \frac{\partial T}{\partial E} = -\frac{1}{kT^2 C_V}. \quad (4.165)$$

We can use these results to expand $\ln p(E)$ about $E = \tilde{E}$ through second order in $(E - \tilde{E})^2$. The result is

$$\ln p(E) = \ln p(\tilde{E}) - \frac{(E - \tilde{E})^2}{2kT^2 C_V} + \dots \quad (4.166)$$

or

$$p(E) = p(\tilde{E}) e^{-(E - \tilde{E})^2 / 2kT^2 C_V}. \quad (4.167)$$

We see that (4.167) is the standard form of a Gaussian distribution (3.118) with $\bar{E} = \tilde{E}$ and $\sigma_E^2 = kT^2 C_V$ as expected.

Vocabulary

composite system, subsystem

equal a priori probabilities

microcanonical ensemble, canonical ensemble, grand canonical ensemble

Boltzmann distribution, Gibbs distribution

entropy S , Helmholtz free energy F , Gibbs free energy G , Landau potential Ω

demon algorithm, Metropolis algorithm

Additional Problems

Problem 4.35. Statistical nature of the Clausius statement of the second law

Discuss the statistical nature of the Clausius statement of the second law that energy cannot go spontaneously from a colder to a hotter body. Under what conditions is the statement applicable? In what sense is this statement incorrect? \square

Problem 4.36. Fundamental nature of the second law

Given our discussion of the second law of thermodynamics from both the macroscopic and microscopic points of view, discuss the following quote:

“The law that entropy always increases, the Second Law of Thermodynamics, holds . . . the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations, then so much the worse for Maxwell’s equations. . . . But if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.” Arthur Stanley Eddington, *The Nature of the Physical World*. \square

Problem 4.37. Another two subsystems

Consider an isolated composite system consisting of subsystems A and B that can exchange energy with each other. Subsystem A consists of three noninteracting spins, each having magnetic moment μ . Subsystem B consists of two noninteracting spins each with a magnetic moment 2μ . A magnetic field B is applied to both systems. (This problem is adapted from Reif.)

- Suppose that the total energy is $E_{\text{tot}} = -3\mu B$. What are the accessible microstates of the composite system? What is the probability $P(M)$ that system A has magnetic moment M ?
- Suppose that subsystems A and B are initially separated from each other and that the magnetic moment of A is -3μ and the magnetic moment of B is $+4\mu$. The systems are then placed in thermal contact with one another and are allowed to exchange energy. What is the probability $P(M)$ that the magnetic moment of system A has one of its possible values M ? What is the mean value of the magnetic moment of system A? \square

Problem 4.38. Two magnetic systems in thermal contact

Consider two isolated systems of noninteracting spins with $N_A = 4$ and $N_B = 16$. Their initial energies are $E_A = -2\mu B$ and $E_B = -2\mu B$.

- What is the total number of microstates available to the composite system?

- (b) If the two systems are now allowed to exchange energy with one another, what is the probability that system A has energy E_A ?
- (c) What is the mean value of E_A and its relative fluctuations of E_A ? Calculate the analogous quantities for system B .
- (d) What is the most probable macrostate for the composite system? \square

***Problem 4.39.** An Einstein solid and a magnetic system

Suppose that system A is an Einstein solid with $N_A = 8$ particles and system B consists of $N_B = 8$ noninteracting spins that can be either up or down. The external magnetic field is such that $\mu B = 1/2$. The magnitude of μB has been chosen so that the changes in the energy of system B are the same as system A , that is, $\Delta E = \pm 1$. The two systems are initially isolated and the initial energies are $E_A = 4$ and $E_B = -1$. What is the initial entropy of the composite system? Remove the internal constraint and allow the two systems to exchange energy. Determine the probability $P_A(E_A)$ that system A has energy E_A , the mean and variance of the energy of each subsystem, the most probable energies \tilde{E}_A and \tilde{E}_B , and the probability that energy goes from system A to system B and from system B to system A . Which system is hotter initially? What is the change in the total entropy of the system? \square

***Problem 4.40.** Number of states of the one-dimensional Ising model

We can determine the number of microstates $\Omega(E, N)$ of the one-dimensional Ising model for small N by counting on our fingers. For example, it is easy to verify that $\Omega(-2, 2) = 2$, $\Omega(0, 2) = 2$, $\Omega(-3, 3) = 2$, and $\Omega(1, 3) = 6$ for toroidal boundary conditions where the last spin is a neighbor of the first spin. The general expression for $\Omega(E, N)$ for the one-dimensional Ising model for even N in the absence of an external magnetic field is

$$\Omega(E, N) = 2 \binom{N}{i} = 2 \frac{N!}{i!(N-i)!}, \quad (i = 0, 2, 4, \dots, N) \quad (4.168)$$

where $i = (E+N)/2$ is the number of pairs of nearest neighbor spins pointing in opposite directions. The energy E is measured in units of J so E is an integer.

- (a) Verify that (4.168) gives the correct answers for $N = 2$ and 4.
- (b) Use the result (4.168) to calculate the free energy for $N = 2$ and 4.
- (c) Derive (4.168) by considering the number of ways that i pairs of antiparallel spins can be placed on a lattice. We will discuss the Ising model in more detail in Chapter 5. \square

Problem 4.41. Partition function of two independent systems

Show that the partition function Z_{AB} of two independent distinguishable systems A and B both in equilibrium with a heat bath at temperature T equals the product of the partition functions of the separate systems:

$$Z_{AB} = Z_A Z_B. \quad (4.169)$$

\square

Problem 4.42. A simple density of states

Suppose that the number of microstates between energy E and $E + \Delta E$ of an isolated system of N particles in a volume V is given by

$$g(E)\Delta E = c(V - bN)^N \left[E + \frac{N^2 a}{V} \right]^{3N/2} \Delta E, \quad (4.170)$$

where a , b , and c are constants.

- Determine the entropy of the system as a function of E , V , and N .
- Determine the temperature T as a function of E , V , and N .
- Determine the energy in terms of T , V , and N .
- What is the pressure as a function of T and $\rho = N/V$? □

Problem 4.43. Derivation of the ideal classical gas equations of state

Discuss the assumptions that were needed to derive the ideal classical gas equations of state, (4.65) and (4.67). □

Problem 4.44. Qualitative behavior of the density of states

Assume that the density of states $g(E) = E^{3N/2}$ for an ideal classical gas in three dimensions. Plot $g(E)$, $e^{-\beta E}$, and the product $g(E)e^{-\beta E}$ versus E for $N = 6$ and $\beta = 1$. What is the qualitative behavior of the three functions? Show that the product $g(E)e^{-\beta E}$ has a maximum at $\tilde{E} = 3N/(2\beta)$. Compare this value to the mean value of E given by

$$\bar{E} = \frac{\int_0^\infty E g(E) e^{-\beta E} dE}{\int_0^\infty g(E) e^{-\beta E} dE}. \quad (4.171)$$

□

Problem 4.45. A simple partition function

The partition function of a hypothetical system is given by

$$\ln Z = aT^4 V, \quad (4.172)$$

where a is a constant. Evaluate the mean energy E , the pressure P , and the entropy S . □

Problem 4.46. An analogy for the heat capacity

The following analogy might be useful for understanding the temperature dependence of the heat capacity of a two state system.

- Suppose that you walk into a store with a few dollars in your pocket, and all the items to purchase cost over \$100. Clearly, you wouldn't be able to buy anything. Would your ability to make a purchase change if somebody gave you an extra dollar?
- Now assume you walked into the same store after winning the lottery. Would your ability to make a purchase change if somebody gave you an extra dollar?

- (c) How much money should you have in your pocket so that an extra dollar would make a difference?
- (d) What is the analogy to the temperature-dependence of the heat capacity of a two state system? \square

Problem 4.47. Qualitative temperature dependence of a two state system

Consider a system of N noninteracting, distinguishable particles each of which can be in single particle microstates with energy 0 and Δ (see Example 4.2). The system is in equilibrium with a heat bath at temperature T . Answer parts (a)–(c) without doing any explicit calculations.

- (a) Sketch the temperature-dependence of the probability that a given particle is in the ground state. Then do the same for the probability that the particle is in the excited state. Discuss the limiting behavior of the probabilities for low and high temperatures. What does high and low temperature mean in this case?
- (b) Sketch the T -dependence of the mean energy $E(T)$ and give a simple argument for its behavior.
- (c) From your sketch of $E(T)$ sketch the T -dependence of the heat capacity $C(T)$ and describe its qualitative behavior. Give a simple physical argument why C has a maximum and estimate the temperature at which the maximum occurs.
- (d) Calculate $C(T)$ explicitly and verify that its behavior is consistent with the qualitative features illustrated in your sketch. The maximum in the heat capacity of a two state system is sometimes called the Schottky anomaly for historical reasons, but the characterization of this behavior as an anomaly is a misnomer because many systems in nature behave as two state systems. \square

Problem 4.48. Qualitative behavior of the heat capacity for a simple system

Consider a system of N noninteracting, distinguishable particles. Each particle can be in one of three states with energies 0, Δ , and 10Δ . Without doing an explicit calculation, sketch the temperature dependence of the heat capacity. \square

Problem 4.49. Mean energy of a two state system

Consider a system of one particle in equilibrium with a heat bath. The particle has two microstates of energy $\epsilon_1 = 0$ and $\epsilon_2 = \Delta$. Find the probabilities p_1 and p_2 when the mean energy of the system is 0.2Δ , 0.4Δ , 0.5Δ , 0.6Δ , and Δ , respectively. What are the corresponding temperatures? (Hint: Write the mean energy as $x\Delta$ and express your answers in terms of x .) \square

Problem 4.50. One-dimensional harmonic oscillators in equilibrium with a heat bath

- (a) Calculate the specific heat (the heat capacity per oscillator) of a system of N one-dimensional harmonic oscillators (see Example 4.3).
- (b) Plot the T -dependence of the mean energy per particle E/N and the specific heat c . Show that $E \rightarrow kT$ at high temperatures for which $kT \gg \hbar\omega$. This result corresponds to the classical limit and will be shown in Section 6.2.1 to be an example of the equipartition theorem. In this limit the energy kT is large in comparison to $\hbar\omega$, the separation between energy levels. Hint: expand the exponential function in (4.132).

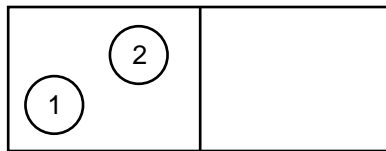


Figure 4.9: The two particles considered in Problem 4.52. The two distinguishable particles can each be in one of the two boxes. The energy of the system depends on which box the particles occupy.

- (c) Show that at low temperatures for which $\hbar\omega \gg kT$, $E/N = \hbar\omega(\frac{1}{2} + e^{-\beta\hbar\omega})$. What is the value of the heat capacity? Why is the latter so much smaller than it is in the high temperature limit? Why is this behavior different from that of a two state system?
- (d) Verify that $S \rightarrow 0$ as $T \rightarrow 0$ in agreement with the third law of thermodynamics, and that at high T , $S \rightarrow kN \ln(kT/\hbar\omega)$. The latter result implies that the effective number of microstates for which the probability is nonzero is proportional to $N e^{kT/\hbar\omega}$. \square

Problem 4.51. The compressibility and fluctuations

We have found that the constant volume heat capacity is related to the variance of the energy fluctuations in the canonical ensemble (see (4.88)). The isothermal compressibility is defined as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T. \quad (4.173)$$

Explain why κ can be interpreted as a linear response. In analogy to the relation of C_V to the energy fluctuations, what type of fluctuations do you think are related to κ at fixed T , P , and N ? \square

Problem 4.52. Consider the system illustrated in Figure 4.9. The system consists of two distinguishable particles, each of which can be in either of two boxes. The system is in thermal equilibrium with a heat bath at temperature T . Assume that the energy of a particle is zero if it is in the left box and r if it is in the right box. There is also a correlation energy term that increases the energy by Δ if the two particles are in the same box.

- (a) Enumerate the $2^2 = 4$ microstates and their corresponding energy.
- (b) Calculate the partition function Z for arbitrary values of r and Δ and use your result to find the mean energy.
- (c) What is the probability that the system is in a particular microstate?
- (d) Suppose that $r = 1$ and $\Delta = 15$. Sketch the qualitative behavior of the heat capacity C as a function of T . \square

Problem 4.53. Grand partition function of a simple system

Consider a system in equilibrium with a heat bath at temperature T and a particle reservoir at chemical potential μ . The system has a minimum of one particle and a maximum of four

distinguishable particles. The particles in the system do not interact and can be in one of two states with energies zero or Δ . Determine the (grand) partition function of the system. \square

Problem 4.54. Constant pressure ensemble

In the text we derived the form of the probability distribution for a system with fixed T , V , and N (the canonical ensemble) and fixed T , V , and μ (the grand canonical ensemble). What is the form of the probability distribution for an equilibrium system with fixed T , P , and N ? This ensemble has no generally accepted name and is not particularly useful for calculations. However, it is useful for doing simulations at a given pressure rather than for a given volume. \square

Problem 4.55. Alternative derivation of the Boltzmann distribution

Consider a system with a given mean energy \bar{E} and a normalized probability distribution P_s , where P_s is the probability that the system is in microstate s with energy E_s . Show that the Boltzmann distribution maximizes the uncertainty or missing information given the constraints that P_s is normalized and the mean energy is specified (see Section 3.11.1). This derivation does not yield a physical interpretation of the parameter β . How would you determine β in terms of the known constant \bar{E} ? \square

Problem 4.56. Demonstration of an entropy-driven transition

The following demonstration illustrates an entropy-driven transition. Get a bag of M & Ms or similar disk-shaped candy. Ball bearings work better, but they are not as tasty. You will also need a flat bottom glass dish (preferably square) that fits on an overhead projector.

Place the glass dish on the overhead projector and add a few of the candies. Shake the dish gently from side to side to simulate the effects of temperature. You should observe a two-dimensional model of a gas. Gradually add more candies while continuing to shake the dish. As the density is increased further, you will begin to notice clusters of hexagonal crystals.

- At what density do large clusters of hexagonal crystals begin to appear?
- Do these clusters disappear if you shake the dish faster?
- Is energy conserved in this system? Do the particles move if you do not shake the dish?
- Compare the behavior of this system (an example of granular matter) to the behavior of a usual gas or liquid. \square

Suggestions for Further Reading

Joan Adler, “A walk in phase space: Solidification into crystalline and amorphous states,” *Am. J. Phys.* **67**, 1145–1148 (1999). Adler and Laird discuss the demonstration in Problem 4.56.

Ralph Baierlein, *Thermal Physics*, Cambridge University Press, New York (1999).

George B. Benedek and Felix M. H. Villars, *Physics with Illustrative Examples from Medicine and Biology: Statistical Physics*, second edition, Springer (2000).

- Carlo Cercignani, *Ludwig Boltzmann: The Man Who Trusted Atoms*, Oxford University Press (1998).
- Brian B. Laird, “Entropy, disorder and freezing,” *J. Chem. Educ.* **76**, 1388–1390 (1999).
- Thomas A. Moore and Daniel V. Schroeder, “A different approach to introducing statistical mechanics,” *Am. J. Phys.* **65**, 26–36 (1997).
- F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1965).
- W. G. V. Rosser, *An Introduction to Statistical Physics*, Ellis Horwood Limited (1982). As far as we know, this book was the first to introduce the Einstein solid in the context of the counting of states and the thermal interaction of simple systems.
- Daniel V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley (1999).
- Ruth Chabay and Bruce Sherwood, *Matter & Interactions*, second edition, John Wiley & Sons (2007), Vol. 1. This introductory text discusses the Einstein solid in the same spirit as our text.
- Jan Tobochnik, Harvey Gould, and Jon Machta, “Understanding the temperature and the chemical potential using computer simulations,” *Am. J. Phys.* **73**(8), 708–716 (2005). This article describes the demon algorithm in detail for use as an ideal thermometer and as an ideal chemical potential meter (see Section 7.2).
- Jan Tobochnik and Harvey Gould, “Teaching statistical physics by thinking about models and algorithms,” *Am. J. Phys.* **76**, 353–359 (2008). This article describes why Monte Carlo simulations give the correct thermodynamic averages and ways of simulating systems more efficiently.